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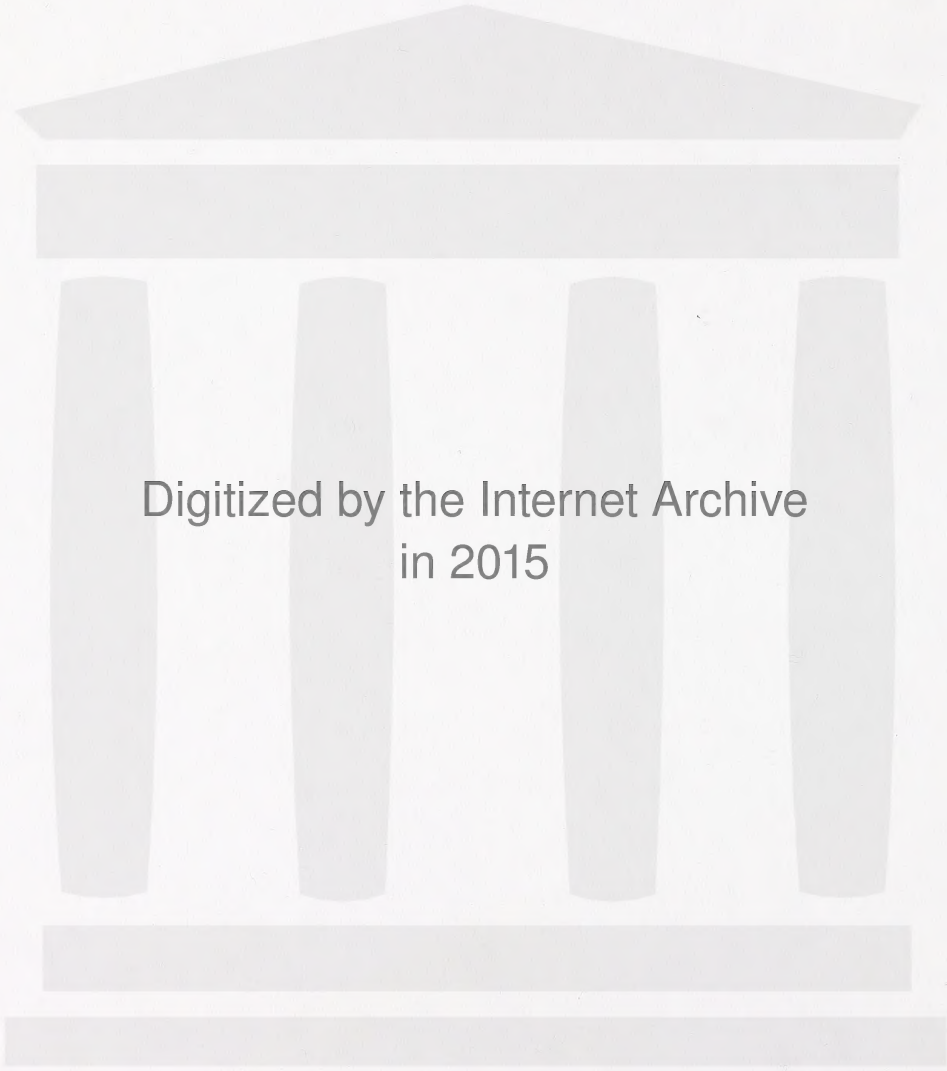
AOSTRA TECHNICAL PUBLICATION SERIES #11

SYNCRUDE ANALYTICAL METHODS MANUAL FOR BITUMEN UPGRADING

Published by

Alberta Oil Sands Technology and Research Authority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SYNCRUDE ANALYTICAL METHODS MANUAL FOR BITUMEN UPGRADING

Edited by

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Alberta
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SYNCRUDE ANALYTICAL METHODS MANUAL FOR BITUMEN UPGRADING

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TABLE OF CONTENTS

1. INTRODUCTORY SECTION

1.1 Acknowledgements 5
1.2 Preface 7
1.3 General Introduction on the Alberta Oil Sands 9
1.4 The Chemical Nature of the Alberta Bitumens 11
1.5 The Commercial Upgrading of Bitumen 23
1.6 Foreword to the Analytical Procedures 35

2. ELEMENTAL ANALYSIS

2.1 The Determination of Carbon and Hydrogen and Catalyst Samples 39
2.2 Metals in Hydrocarbon Analysis by ICAP-AES 45
2.3 Simultaneous Determination of Nitrogen and Sulphur by Chemiluminescence and Fluorescence 49

3. HYDROCARBON CHARACTERIZATION

3.1 Existent Dry Sludge by Hot Filtration Test 57
3.2 Extraneous Material by Filtration 63
3.3 Determination of the Specific Gravity and Density of Bituminous Materials by Pycnometer 67
3.4 Determination of Hydrocarbon Density Using the Anton Parr Densimeter 71
3.5 Determination of the Refractive Index of Hydrocarbon Liquids 73
3.6 Determination of Microcarbon Residue (MCR) of Bitumen, Heavy Gas Oils, and Light Gas Oils 77
3.7 Determination of the Kinematic Viscosity of Transparent and Opaque Liquids 81
3.8 Determination of Bromine Number for Liquid Petroleum Hydrocarbons by the Electrometric Method 85
3.9 Supercritical Fluid Chromatography Analysis of Aromatic Content of Petroleum Products 91

4. DISTILLATION

4.1 Simulated Distillation of Petroleum Products 97
4.2 The Spinning Band Distillation of Liquid Hydrocarbons and Bitumen 103
4.3 D1160 Automatic Distillation of Bituminous Material 119

5. CATALYST CHARACTERIZATION

5.1 Elemental Analysis of Syncrude Process Catalysts 131
5.2 Measurement of Catalyst Crush Strength 137
5.3 Determination of Loss on Attrition of Fresh Hydrocracking Catalyst 141
5.4 Determination of Compacted Bulk Density of Catalyst 143
5.5 Length and Diameter of Catalyst 145
5.6 Determination of the B.E.T. Surface Area by the Continuous Flow Method 147
5.7 Pore Size Distribution and Total Pore Volume of Catalyst Materials by Mercury Intrusion 155
5.8 Determination of Surface Area, Nitrogen Pore Volume, and Pore Size Distribution of Catalysts by Micromeritics ASAP-2000 161

6. MISCELLANEOUS

6.1 Quantitative Analysis of Refinery Gases by Gas Chromatography 167

7. APPENDIX

7.1 The Syncrude-AOSTRA Air Quality Prediction System: An Early Warning System for Air Quality 181

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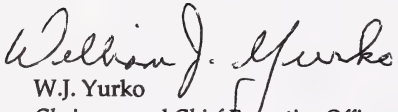
PUBLISHER'S NOTE

AOSTRA TECHNICAL PUBLICATION SERIES NUMBER 11

AOSTRA is pleased to publish this eleventh book in a series of special publications by industry and academic authors. Like its predecessors, *Syncrude Analytical Methods For Oil Sand and Bitumen Processing; The Thermodynamic and Transport Properties of Bitumens and Heavy Oils; Aquathermolysis: A Synopsis of Work on the Chemical Reaction Between Water (Steam) and Heavy Oil Sands During Simulated Steam Stimulation; Oil Sands Composition and Behaviour Research; A Review of Analytical Methods For Bitumens and Heavy Oils, The Alberta Committee on Oil Sands Analysis; AOSTRA Technical Handbook on Oil Sands, Bitumens and Heavy Oils;* and *Resource Characterization of the McMurray/Wabiskaw Deposit in the Athabasca Central Region of Northeastern Alberta,* this publication is designed to make available, research results, analytical procedures, and engineering data on the properties and behavior of Alberta petroleum resources that may otherwise not be available to the public.



W.J. Yurko
Chairman and Chief Executive Officer
Alberta Oil Sands Technology and Research Authority

Edmonton, Alberta, Canada
October 1991

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The Editors would also like to thank the authors and editors who have kindly permitted us to use figures from their publications. Specific acknowledgements are given, as footnotes, in the text.

Finally, at AOSTRA, where the manuscript of our book was put into its final form for the printers, the Editors want to acknowledge the invaluable assistance of Ms. Diane B. Teppan, Manager of Publications, and Ms. Rachel Recto, without whose skillful efforts, this volume would not have appeared in print.

1

INTRODUCTORY SECTION

Preface

The largest of the oil sands deposits in northern Alberta is the Athabasca. This vast bitumen resource extends over 46,800 square kilometres, and contains close to one trillion barrels of bitumen. Roughly 10% of the resource is covered with less than 45 metres of overburden, and is therefore amenable to surface-mining.

In industrial mining operations, the bitumen must first be extracted from the mined oil sand, and then further processed by upgrading to produce a "synthetic"crude, capable of being handled in standard refineries. The goal of the various commercial upgrading processes is to produce from the bitumen a material with a higher atomic hydrogen-to-carbon ratio and a lower average molecular weight. Such treatments are also designed to reduce the sulphur, nitrogen, and heavy metal content in the synthetic crude product.

The extraction of bitumen from the mined oil sand, and the subsequent upgrading of the recovered bitumen to a product suitable for pipelining, and further refinery processing, are both very large-scale operations, as practised by Syncrude Canada, in the Athabasca deposit. Furthermore, both types of processes are subject to increasingly strict environmental requirements.

Process control at Syncrude Canada for both extraction and upgrading depends strongly upon reliable analytical procedures. The analytical chemists at the Syncrude research laboratories are constantly engaged in research into new analytical methods, and into improvements in current ones.

The first volume in this series on Syncrude analytical methods was published in 1979.[1] It covered a representative collection of procedures in use at that time for monitoring oil sand and bitumen processing, including the hot water extraction process, subsequent froth treatment and also bitumen upgrading.

The present volume places emphasis upon analytical sequences used in evaluating upgrading processing of the recovered bitumen.

Each method described has been carefully revised and brought up-to-date by the analytical chemists at Syncrude Research in Edmonton.

As with the first volume in this series, the analytical methods presented here are donated by Syncrude as a service to the oil sands industry in general.

In addition, in the present volume, efforts have been made to produce a book which can be used as an analytical laboratory manual in universities and technical schools for laboratory courses in petroleum chemistry. To this end, an introductory chapter has been included covering the chemical nature of the Alberta bitumens — a field in which a great deal of important research is being done at the present time on the vast range of chemical compounds in the bitumen, and on how these chemical structures can be used to trace the specific biological origins of this complex natural mixture.

The present volume again represents a cooperative effort between AOSTRA and Syncrude Canada. Analytical research is considered by AOSTRA as a vital factor in the commercial development of the oil sands, and AOSTRA is pleased to be able to cooperate once more with Syncrude Canada by making this present volume of thoroughly-tested analytical methods available to the oil sands industry and to educational institutions for training analytical chemists and technicians.

Finally the following points should be noted relevant to the use of the procedures described in this volume:

1. Analytical methodologies for monitoring the processing of oil sand and recovered

[1] "Syncrude Analytical Methods for Oil Sands and Bitumen Processing," published by The Alberta Oil Sands Technology and Research Authority, Edmonton, Alberta, Canada (1979).

bitumen have improved markedly since the publication of the first volume in this series, 12 years ago. Nevertheless Syncrude Research is convinced that a great deal of research is still required before a full range of thoroughly reliable analytical procedures is available to the oil sand industry.

2. While Syncrude has expended a great deal of effort to ensure that the procedures herein described give reliable results, similar accuracy cannot be guaranteed to others who use these methods.
3. While AOSTRA welcomes this volume as an important step in the process of standardizing oil sand analytical procedures, the Authority does not necessarily sanction the methods for general use.
4. Each procedure lists certain safety precautions. These lists are not meant to be exhaustive; rather they are intended to make note of safety requirements peculiar to each procedure. Normal laboratory safety practice has been assumed in every case. Toxicity data for bitumen and the many streams generated during processing are still incomplete. Good safety practice is ensured by minimizing exposure to such materials.
5. In the description of apparatus, reagents, and materials, only information related to quality or size is provided where many sources of supply exist. For specialized items and major equipment, the manufacturer whose product was used is specified. This information is provided solely for the purpose of defining the actual analytical practice, and is not necessarily an expression of recommendation. Certain of the equipment listed may be protected by patent and trademark rights. The burden is on the users of these methods to avoid infringing such protection.
6. Certain methods published by the American Society For Testing Materials (ASTM), Universal Oil Products (UOP), and some manufacturers of chemical instrumentation have formed the basis for some of the methods described in this volume. A general acknowledgement is hereby given to these sources: separate acknowledgements are made in the literature references for individual methods.

General Introduction on the Alberta Oil Sands

Oil sand, also known as tar sand, consists of a mineral sand matrix impregnated with bitumen — a heavy and viscous carbonaceous material.

Deposits of oil sand are found throughout the world; their size ranging from local outcrops to major geological features. As previously noted in the Preface, the Athabasca deposit, located in northeastern Alberta, Canada, is the largest known deposit. It covers an area of 46,800 square kilometres and contains an estimated 137 billion cubic metres (862 billion barrels) of oil. The oil-bearing formation has a thickness of up to 45 metres. It is covered with overburden material ranging from 0 to 750 metres in thickness. The oil-bearing layers are typically not visible, except where they have been exposed, such as along river banks.

In an oil sand formation, the individual sand particles can either be in direct contact with the bitumen, or they can be separated by a water layer. In the latter case, the bitumen is in contact only with the water, and not with the particles themselves. This situation is illustrated schematically in Figure 1. This distinction makes a crucial difference from a processing point of view. Water-wet oil sand is readily amenable to extraction using the Hot Water Process, originally developed by K.A. Clark.[1] Oil sand from the Athabasca deposit is water-wet, whereas many other deposits, such as those in Utah, Alabama, and California are oil-wet.

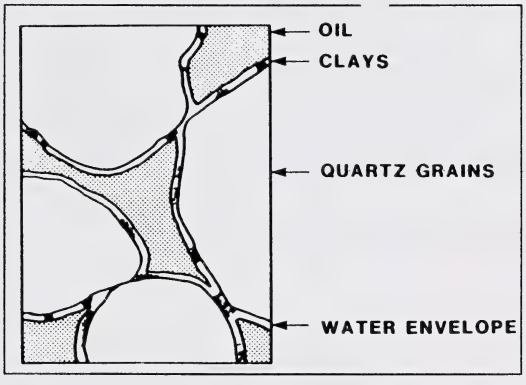


Figure 1. Schematic structure of water-wet Alberta oil sands. (Reprinted with permission from: R.W. Luhning and A.W. Hyndman, The Journal of Canadian Petroleum Technology, 30, no. 2 (1991), p. 66, Figure 11 and The Canadian Institute of Mining, Metallurgy and Petroleum.)

Currently two plants, operated respectively by Syncrude and Suncor, are producing synthetic crude oil from the Athabasca deposit. Worldwide, these are the only large scale and integrated plants producing synthetic crude oil from an oil sand deposit. The combined production — 35,800 cubic metres per day (225,000 bpd) — of these two plants exceeds 15% of the total Canadian crude oil requirements.

1 K.A. Clark and D.S. Pasternak, "The Hot Water Separation of Bitumen from Alberta Bituminous Sand," Ind. Eng. Chem., 24, (12), (1932) pp. 1410–1416.

These plants are fully integrated, including the mining of the oil sand, the extraction of the bitumen from the sand, and the upgrading of the recovered bitumen into a synthetic crude oil.

Since bitumen is not free-flowing, it cannot readily be pumped from the formation, as is done for conventional crude. Where the oil sand formation is close to the surface, the overburden material can be stripped, and the oil sand can be mined by open-pit mining. This is the approach taken at the Syncrude and Suncor plants, since both are located in an area of relatively shallow overburden.

For deeper oil sand formations, where overburden stripping is no longer economical, in-situ recovery techniques are being developed and tested by several operators. These methods usually use steam injection or underground combustion for reducing the viscosity of the oil, so that it can be pumped to the surface.

Currently none of the in-situ plants are fully equipped with upgrading facilities. Upgrading of the produced bitumen is performed off-site. The largest in-situ plant in Alberta is located in the Peace River area, in the Carbonate Trend, and produces about 800 cubic metres per day (5000 bpd).

Finally it should be noted that Alberta is also developing commercial upgrading facilities for the heavy oil[2] produced in the Lloydminster area of Alberta. An upgrader, costing roughly $1.3 billion, is under construction at Lloydminster, with funding provided jointly by Husky Oil Ltd. and the Governments of Canada, Alberta, and Saskatchewan.

2 For the distinction between heavy oil and bitumen, see Section 1.4 of this book entitled, "The Chemical Nature of the Alberta Bitumens."

The Chemical Nature of the Alberta Bitumens

INTRODUCTION

From the standpoint of their number and diversity, the chemical compounds present in the bitumens of Alberta rival the vast collection of plants growing in the rain forests of the Amazon. In fact, it is generally recognized that bitumen ranks among the most complex chemical mixtures to be found in nature.

By way of definition, it is important to distinguish between the heavy crude oils found in Alberta, and throughout the world, and the tar sand oils, or bitumens as they are called here. These distinctions are made primarily on the basis of viscosity. Heavy crude oils have a gas-free viscosity from 100 to 10,000 mPa·s (centipoises), at original reservoir temperatures, while tar sand oils, or bitumens, have gas-free viscosities from 10,000 to several million mPa·s (centipoises) at original reservoir temperatures.

Determining the precise atomic arrangements in the molecules for the enormous number of chemical compounds that make up the Alberta bitumens have required a great deal of creativity and skill on the part of structural chemists, using the most sophisticated methods available to modern chemical science. However, great progress has been made in this field in the past 20 years, largely due to new methods for separating complex organic mixtures into simpler and more tractable ones, and for determining the types of molecular structures present.[1]

In addition to a very large range of simple to complex hydrocarbons, bitumen contains appreciable amounts of asphaltenes and resins. These latter materials are partially polymeric systems of high molecular weight which exist largely in colloidal form, together with strongly polar substances in the lower molecular weight region. There are also present significant quantities of organic compounds containing heteroatoms, such as sulphur, oxygen, and nitrogen, as well as organometallic compounds, and some clay minerals; most of these latter compounds form part of the asphaltenes and resins.

The elemental range of compositions for Alberta oil sand bitumens is shown in Table 1.

Table 1. Elemental range of compositions for Alberta oil sand bitumens

H/C atomic ratio:	1.46–1.50				
Weight percent composition					
carbon:	81–84	hydrogen:	10.0–11.0	nitrogen:	0.3–0.6
oxygen:	0.8–1.65	sulphur:	4.6–5.6	ash:	0.5–1.0
nickel:	60–100 (mg/kg)	vanadium:	160–300 (mg/kg)		

The percentages of the various elements in the bitumens give very little information indeed concerning the treasure-house of chemical compounds contained therein. Locked within the bitumen is the complete geochemical history of the material, as well as a gigantic collection of unique chemicals for which many special uses will undoubtedly be found in the future.

There are two major incentives for studying the detailed chemistry of petroleums, of which bitumens are the most viscous member. Firstly, a knowledge of the chemical structures present in these fossil resources provides vital information on their biological origins, and on the changes that have taken place in them over geological time. And what is

1 For a much more detailed discussion of the general subject matter of this chapter, see: O.P. Strausz, "Bitumen and Heavy Oil Chemistry," which forms Chapter 3 of "The AOSTRA Technical Handbook on Oil Sands, Bitumens and Heavy Oils," published by The Alberta Oil Sands Technology and Research Authority, Edmonton, Canada (1989).

of great practical importance, such data can be very valuable in predicting where yet-undiscovered petroleum deposits might be found. Secondly — and much more relevant to the subject matter of the present book — the changes that take place in the properties of bitumens, for example, during the various upgrading processes in current use, are chemical changes, and the more we know about the chemical compounds present in the bitumen, and their modes and rates of decomposition, the greater will be our chances of designing upgrading processes which fully utilize these vital petrochemical resources. Furthermore, many of the chemical compounds present in bitumens may well have special uses for the manufacture of products for the chemical and pharmaceutical industries. From our increasing knowledge of the chemistry of the bitumens, methods will undoubtedly be found for recovering these higher-value chemicals from the bitumens, before the remainder is consigned to the production of fuels and related uses.

ANALYTICAL CLASSIFICATION OF THE BITUMENS

In the bitumen processing industries, it is common practice to classify bitumens by SARA analysis, in which, as the initials indicate, the bitumen is analyzed into four fractions — the Saturates, the Aromatics, the Resins, and the Asphaltenes. This type of group analysis is very valuable in characterizing bitumens prior to upgrading. It is, however, of less value for determining the precise chemical species present in the bitumen.

For detailed chemical studies of bitumen, advantage is taken of the fact that bitumen is totally soluble in benzene or methylene chloride. When an excess of *n*-pentane is added to this solution, the so-called asphaltenes are precipitated. What remains in solution are termed the maltenes. The asphaltenes constitute some 15–20 wt% of the bitumen, with the maltenes making up the remainder. The maltenes can be further separated into three fractions: the saturates, the aromatics, and the resins. A brief description of the current status of our knowledge of the molecules present in the three maltene fractions and in the asphaltenes follows.

TYPES OF SATURATED HYDROCARBONS IN THE MALTENES

The chemical makeup of the large maltene fraction of Athabasca bitumen has been the subject of a classic series of investigations by O.P. Strausz et al., which was published in the AOSTRA Journal of Research in the period, 1985–86.[2] For their investigations they used, as raw material, part of a large bituminous sand lot collected by Syncrude Canada Ltd. near Fort McMurray, Alberta, Canada in 1975. The sand lot was recovered from a mineable area, 18 m below the surface.

The bitumen was extracted from the tar sand with CH_2Cl_2, and the asphaltene fraction was then precipitated from the extract with a large excess of *n*-pentane. The yields of asphaltene and maltene were 17 and 83 wt%, respectively.

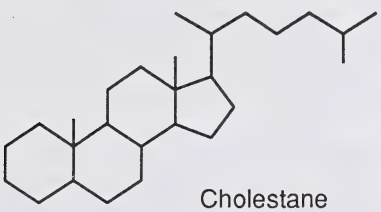
The maltene fraction was separated into 15 fractions, by general chemical type, using elution chromatography and appropriate solvents. All but one of the 15 fractions were molecularly distilled, using a sublimation apparatus operating at 10^{-3} Torr, and up to a temperature of 240°C. Molecules up to a carbon number of C-50 would sublime under these conditions. The first fraction, the largest one in volume, was recognized as primarily saturated hydrocarbons. This fraction constituted about one-third of the maltene. Strausz et al. further purified this fraction which reduced its volume to about one-fifth of the original maltene. This material was examined by field ionization mass spectrometry, which has the advantage over other mass spectrometric techniques of producing primarily parent ions, without significant decomposition.

All hydrocarbons can be represented by the general formula, C_nH_{2n+z}, where z can

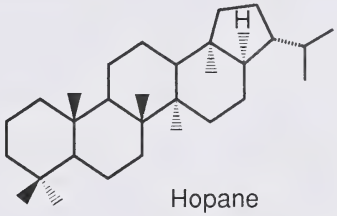
[2] J.D. Payzant, A.M. Hogg, D.S. Montgomery, and O.P. Strausz, AOSTRA J. Res. 1 (1985) p. 175, 183, 203; T.W. Mojelsky, D.S. Montgomery, and O.P. Strausz, Ibid., 2 (1986) p. 25.

have values of 2, 0, –2, –4, etc., in decrements of 2. A z-value of +2 indicates an open-chain saturated hydrocarbon. For saturated hydrocarbons, z-values of 0, –2, –4, –6, –8, and –10 denote saturated hydrocarbons with 1–, 2–, 3–, 4–, 5–, and 6– rings, respectively.

For the purified saturated hydrocarbon fraction, it was found that most of the hydrocarbons had z-values in the 0 to –8 range. Four-ring and five-ring hydrocarbons were shown to be particularly abundant at and near the C-30 carbon number. Those hydrocarbons with a smaller number of rings were more plentiful at lower carbon numbers. It should be noted that Strausz et al. identified a prominent $C_{27}H_{48}$ compound as the sterane known as cholestane, and another at $C_{30}H_{52}$ (z = –8) as hopane.

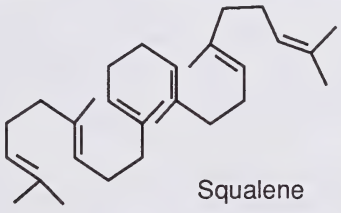


Cholestane



Hopane

Both the steranes and hopanes are known to be built up in living organisms from isoprene units. An example of this type of biosynthesis involves an acyclic hydrocarbon occurring up to 90% in the liver oils of certain sharks. It is called squalene, $C_{30}H_{52}$. It is an open-chain hexamer of 2-methyl-1, 3-butadiene or isoprene.



Squalene

It is known that squalene can be cyclized, in vivo, in bacteria and in certain algae, to produce hopane derivatives, and in higher organisms, steranes. Squalene is also considered to be an important intermediate in the biosynthesis of the fundamental steroid, cholesterol. Thus we have further evidence of the specific biological origin of the bitumens.

It is appropriate at this point to note that we are now dealing with a very important broad class of compounds closely identified with the chemical processes occurring in plants and animals. These are known as the terpenes, with the name originating from the Greek word for the turpentine tree, since many of the volatile members form part of the characteristic odours of plants and flowers. The terpenes are now recognized as being biosynthetic products from isoprene units, C_5H_8. The structure of squalene, above, represents a higher member of the terpene family.

The terpenes include not only hydrocarbons, but also products that can be derived from the parent $(C_5H_8)_n$ structures without changing the number of carbon atoms in the molecule. Many of the terpene alcohols and aldehydes are very important odourants and flavour agents. In general, then, the terpenes have carbon numbers of $(C_5)_n$, where n can have values of 1, 2, 3, 4, etc. This large and varied class of compounds is divided into hemiterpenes, C_5; terpenes, C_{10}; sesquiterpenes, C_{15}; diterpenes, C_{20}; triterpenes, C_{30}; tetraterpenes, C_{40}; etc. Natural rubber, an isoprene polymer, would be a high molecular weight polyterpene.

We will encounter terpenoid structures again in the resin fraction of bitumen.

The saturated fraction of the maltenes in Athabasca bitumen consist, almost entirely, of cyclic structures containing one to six rings with a moderate maximum at z = –2, corresponding to dicyclic hydrocarbons. Similar results have been found for bitumens from other areas in northern Alberta.

Conventional light crude oils differ particularly from the bitumens in that the former have high concentrations of paraffinic hydrocarbons, which are open chain, or acyclic molecules with z = +2. It is a well established fact in microbiology that microorganisms, which feed on crude oils, attack, by oxidation, first the straight-chain paraffins, then branched-chain ones, and continue to oxidize hydrocarbons with more negative values of z, ultimately leading to the final products, carbon dioxide and water. This type of microbiological degradation satisfactorily accounts for the presence of hydrocarbons with negative value of z, which are found in the saturate fraction of the maltenes in bitumen. It is generally agreed that the maltene fraction shows strong evidence of having been derived, at least in part, from mature paraffinic crudes by bacterially-induced changes taking place over long periods of time.

In short, we now have a plausible geochemical explanation of how the many homologous series of cycloparaffins, which dominate the saturate fraction of the maltenes in bitumen, were created in the past. We can envision reservoirs of mature crude oils, with their very high concentrations of open-chain paraffins, being contacted for a limited period by microorganisms which tended to favour *n*-paraffins for their food supply. Now even mature crudes contain appreciable levels of cycloparaffins and it seems reasonable to conclude that the highly-enriched cycloparaffin levels in the maltenes of the bitumen could have resulted from the total microbiological oxidation of the open-chain paraffins to carbon dioxide and water, leaving behind the less favoured cycloparaffins to form the saturate fraction of the maltenes. In general the laboratory evidence, from studying bacteria which feed on crude oils, indicates that these oxidative attacks are quite fast and occur not only on open-chain paraffins but also on the alkyl sidechains of alicyclic and aromatic compounds. One net result of this type of prolonged degradation would be a decrease in the atomic H/C ratio in the oil. And, of course, this ratio is decidedly lower in the bitumens than in mature, paraffinic crudes.

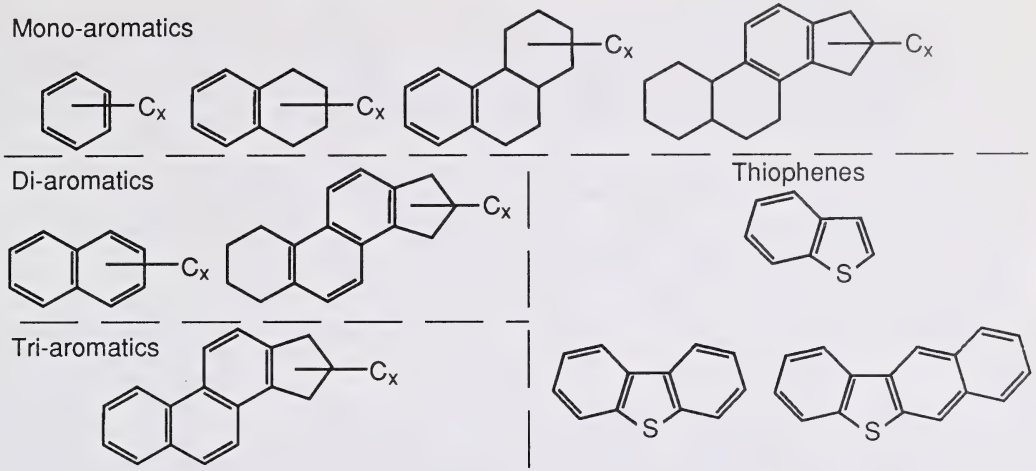
We can reasonably conclude, therefore, that bitumens are, to a significant extent, the product of microbiologically-degraded crude oils. It is by studies such as these that scientists gradually unravel the complex geochemical history of our petroleum deposits.

THE AROMATIC COMPOUNDS IN THE MALTENES

Detailed examination of the aromatic fraction of the bitumen revealed that mono-aromatic types comprised some 10% of the total bitumen; while the di- and trinuclear aromatics took up an additional 9%. The mass spectral data showed conclusively the presence of compounds in which sulphur, and to a much lesser extent, nitrogen, form part of the aromatic system.

The aromatics were found to be present in the maltenes as homologous series stretching beyond C-50. Molecules with more than one aromatic ring cannot be separated by chromatography into aromatic hydrocarbons and the sulphur-containing aromatic thiophenes. The sulphur occurs as benzothiophenes, dibenzothiophenes, and naphthobenzothiophenes. There are also small amounts of aromatics with two sulphur atoms. The remaining sulphur is present as alicyclic sulphides with high H/C ratios indicating near saturation. In addition, small amounts of nitrogen-containing aromatics were also detected.

The structures of some of the prominent types of homologous series of aromatics identified are given here, together with some representative first members of thiophenic series shown to be present in the aromatic fractions.



CHEMICAL COMPOUNDS IN THE RESINS OF ALBERTA BITUMENS

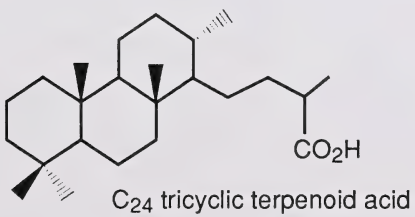
The resins form the largest fraction of the bitumens and, in terms of chemical characterization, they represent a formidable challenge indeed. The molecular weight covers the range 400–6000, and includes heterocyclic compounds, organometallics, and carboxylic acids.

The presence of oxygen-containing heterocycles, as well as carboxylic acids, would suggest the intervention of atmospheric oxidation in the geochemical history of this bitumen.

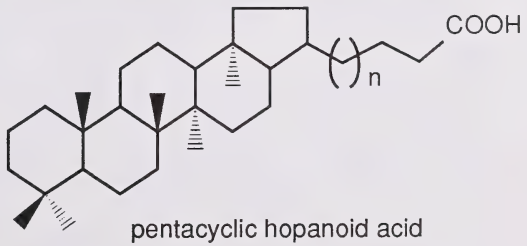
The carboxylic acids in total only represent about 1–2% of the bitumen. However they do have a marked effect on the physical behaviour of bitumen particles toward inorganic surfaces such as sand. Thus Takamura[3] has shown that an aqueous film is held in place between the sand and the bitumen by a repulsive electrical double layer involving the negatively-charged sand and the like-charged bitumen. The negative charge on the bitumen is attributed mainly to the dissociation of carboxylic acids at its surface producing anionic negativity.

The repulsive double layer between the sand and bitumen particles which retains the water layer in place is also responsible for facilitating the separation of the bitumen from the sand in commercial bitumen recovery operations.

The carboxylic acids in the resins have been fairly well characterized (see ref. 1) as mainly tricyclic terpenoid acids and pentacyclic hopanoid acids, the former in the C_{20}–C_{26} range and the latter in the C_{30}–C_{47} range. Representive structures for these acids are given below:



C_{24} tricyclic terpenoid acid

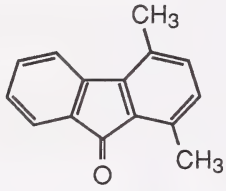


pentacyclic hopanoid acid

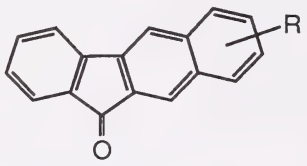
Further evidence of oxidation in the reservoir comes from the identification of a series of oxygen-containing aromatics. Specifically, a series of methyl fluorenones was found, with

3 K. Takamura, AOSTRA J. Res., 2 (1985) p. 1 and references in that article.

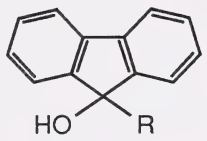
1,4-dimethylfluorenone as the major component. In addition, a homologous series of alkyl benzofluorenones and 9-*n*-alkylflurorene-9-ols were also detected. The actual compounds can readily be obtained in the laboratory by the oxidation of the parent hydrocarbons, fluorene and 9-alkylfluorene. These findings provide further evidence of oxidation reactions occurring in the reservoir. Structures for the molecules discussed are given below:



1,4–dimethyl-
fluorene–9–one

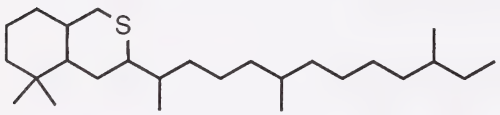


alkylbenzo-
fluorenone

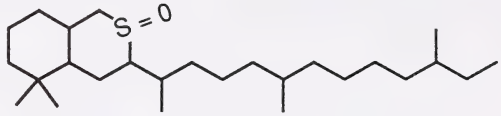


9–*n*–alkyl-
fluorene–9–ol

Another very important group of molecular types encountered in the resin fraction was the cyclic sulphides, and their corresponding sulphoxides. These included terpenoid structures with 2 to 6 rings. In addition, an interesting new series of hopanoid sulphides was discovered. The dicyclic terpenoid sulphides were examined in the C_{12} to C_{26} range, with maximum abundance shown to be at C_{13}. The structure of the C_{26} member of this class of sulphides is shown below together with its sulphoxide.



C_{26} dicyclic terpenoid sulphide



C_{26} dicyclic terpenoid sulphoxide

It should be noted that most of the sulphides encountered can be readily converted to the corresponding hydrocarbons using Raney nickel desulphurization.

This broad group of sulphur-containing molecules has recently been shown to be widely distributed in crude oils and bitumens. Thus they can be found in all Alberta petroleums, as well as in the conventional and heavy oils of Argentina and Venezuela. In fact, it appears now that they are ubiquitous components of all sulphur-containing crude oils.

The cyclic sulphides are known to change by aerial oxidation to their sulphoxides, and this type of reaction can be used to determine the redox conditions in a particular reservoir. Furthermore, the "aging" of tar sand samples from atmospheric exposure can be monitored with this sulphide-to-sulphoxide reaction.

The nitrogen-containing compounds in the resins are all nitrogen heterocycles and cover quite a wide range of structures. They are more important than their concentrations would indicate. One group, the quinolines, cause serious poisoning problems with hydrodesulphurization and hydrogenation catalysts, as well as inducing polymerization and gum formation in the storage of crude distillates.

There are many chemical compounds yet to be characterized in the bitumen resins, most of which are in the undistillable residues. Methods, however, are being developed to explore the molecular configurations in even these intractable materials.[4]

THE CHEMICAL MAKEUP OF THE ALBERTA ASPHALTENES

As has been pointed out earlier, about 15–20 wt% of Alberta bitumens are asphaltenes.

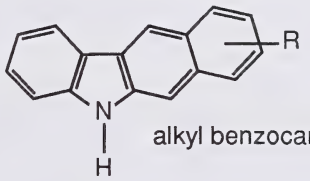
4 T.W. Mojelsky, D.S. Montgomery, and O.P. Strausz, AOSTRA J. Res. 2 (1985) p. 131, 3 (1986) p. 177.

This complex material has the highest mean molecular weight of all the bitumen fractions. The crude asphaltene can be precipitated from a benzene or methylene chloride solution of the bitumen by adding a 40- to 50-fold excess of *n*-pentane. In appearance, the precipitated asphaltene is a dull, brownish-black, amorphous solid. When prepared by evaporation of a solution in benzene or methylene chloride, the asphaltene is obtained as a brittle, shiny-brown film.

After repeated centrifugations to remove ash, it is found that the number average molecular weight of the purified material is approximately 3600. Gel permeation chromatography can be used to partition the asphaltene, by molecular weight, into five fractions, ranging from 1200 to 16,900 m.w. units. The quantities in the various fractions show that over 50% of the asphaltene has an m.w. exceeding 13,000. Thus it can be seen that we are dealing here with a material composed, to a major extent, of giant molecules which would be extremely difficult to characterize individually. Despite these difficulties, a great deal has been learned in recent years about the chemical attributes of these large molecular aggregates.

Before proceeding to a discussion of the high m.w species in bitumen, it should be noted that the low m.w. end of the asphaltene has recently been examined, and a number of homologous series have been identified. This has been done by extracting the asphaltene with acetone, which dissolves out the lowest m.w. material with a number average of about 1200. This extract amounts to about 20% of the total asphaltene.

One group of series identified were all highly-substituted carbazoles, and corresponded to about 0.4 wt% of the bitumen. The parent nitrogen heterocycle, carbazole, is a well-known component of coal tar. The structure for one major series is shown below:



alkyl benzocarbazole

Among the sulphur-containing compounds identified in the acetone-extract were terpenoid sulphides and sulphoxides which were first detected, it will be recalled, in the resin fraction. These carry-over compounds from the resin fraction only amounted to about 0.5 wt% of the asphaltene. Higher m.w. sulphur-containing structures were also detected, but these have not yet been characterized.

Finally, quite a number of other types and series of compounds came to light in this examination of the acetone extract. These included several series of carboxylic acids and fluorenones, together with other related oxygenated compounds. Those interested in following this interesting investigation in detail should consult reference 1.

Let us return now to the dominant constituents in asphaltene, namely the giant molecules which mainly give the asphaltene its unique properties.

By using spectroscopic methods (NMR, MS, IR) coupled with specialized oxidative probes, it has been possible to tie down fairly conclusively certain characteristics of the large molecular aggregates in the asphaltenes. These attributes can be summarized roughly as follows:

(a) There are both aromatic and naphthenic main cores to these molecular systems.

(b) To these cores are attached *n*-alkyl sidechains. Both the aromatic and naphthenic centres have joined to them *n*-alkyl sidechains stretching out to 34 carbons, and beyond, in length.

(c) The aromatics cores are often hooked together with *n*-polymethynene bridges, extending to, at least, 22 carbons.

(d) *n*-Polymethylene bridges also serve to tie together aromatic and naphthenic cores with these bridges involving up to 35 carbons.

(e) While some of the sulphur present is tightly bonded as aromatic thiophenes, an important fraction of the sulphur is in the form of the much more labile non-aromatic sulphides, where the C-S bonds represent a point of thermal rupture for these molecular structures.

(f) The aliphatic portions of these giant molecules show an enormous range of molecular weights, stretching far beyond the number average for the asphaltene in toto.

(g) The long *n*-alkyl chains attached to the aromatic cores will tend to decompose on thermolysis at the benzyl carbon, because of the resonance stabilization of the benzylic free radical.

There are many other fascinating characteristics of the great molecular aggregates in the asphaltenes. For example, large stable free radicals have been repeatedly detected by Electron-Spin Resonance spectroscopy. These indicate the presence of condensed aromatic rings among the aggregates. In addition, porphyrins are present which can also be readily detected by ESR spectroscopy. The significant amounts of vanadium in the asphaltene are at least partly present as porphyrin complexes.

Another interesting characteristic of these big molecules pertains to the nature of the "cores." Recent studies indicate here that the large polynuclear aromatic units, formerly thought to be dominant, are in fact relatively infrequent. Present findings suggest rather that the aromatic cores contain, on the average, no more than three rings.

Structurally we can envision a complex reticulum of aromatic and naphthenic cores held together by polymethylene springs, and bridged with an occasional sulphur atom forming a five- or six-membered ring. The cores also bristle with *n*-alkyl sidechains of varying lengths. In the natural state, these massive structures would be entangled with porphyrins, clay particles, and the higher molecular weight members of the resin family of compounds

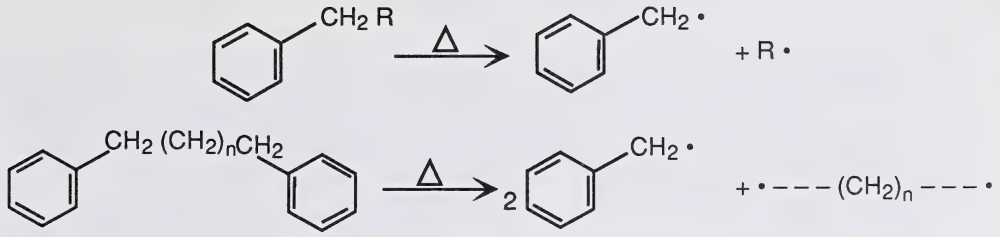
From the above it can be seen that a great deal has been learned about the general characteristics of these giant molecules which dominate the asphaltenes. Such closely-packed structures obviously are major contributors to carbonization in thermal upgrading processes.

SOME PROBABLE CHEMICAL CHANGES DURING BITUMEN UPGRADING

The upgrading of bitumen to produce various commercial products starts with two general types of processes. These are (a) thermal upgrading methods which reduce the viscosity of the bitumen and lead to carbon rejection, and (b) thermal processing of the bitumen in the presence of high pressures of hydrogen and a catalyst, to reduce carbon rejection, and increase the atomic H/C ratio of the final product. The specific commercial processes currently in use in upgrading are discussed in some detail in the next section of this book.

Here we would like to utilize our knowledge of the chemical compounds known to be present in bitumen, as briefly described in this chapter, together with insights from the vast field of chemical kinetics, to propose some types of reactions which probably occur during the commercial upgrading of bitumens (see also ref. 1).

In discussing the heavy ends of the maltenes, and the asphaltenes, it has already been noted that there are many molecules which have *n*-alkyl sidechains attached to aromatic cores, as well as those with aromatic cores tied together by *n*-polymethylene bridges. It is a well-established fact that these structures tend to rupture, upon heating, at the first carbon beyond the aromatic core, referred to, as noted earlier, as the benzylic C-C bond. This is true because the benzylic bond is some 7–8 kcal/mole weaker than normal C-C bonds. The following reactions illustrate this important fact:



The dot after the products in the above reactions indicates the unpaired electron identifying a free radical, and it is well established that these highly reactive intermediates can lead to a range of products of lower molecular weight than the parent molecules from which they broke off. Some of the more obvious types of reactions follow:

(1) $R\bullet \longrightarrow$ 1-alkene + $H\bullet$

(2) $R'\bullet + R''\bullet \longrightarrow$ *n*-alkane + 1-alkene

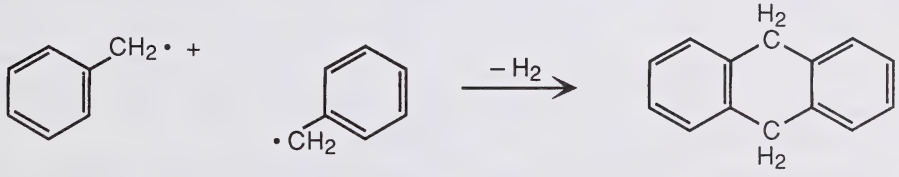
(3) $R'\bullet + R''H \longrightarrow$ *n*-alkane + $R''\bullet$

(4) $R\bullet \longrightarrow R'\bullet + C_2H_4$

Step (1) is the unimolecular loss of a hydrogen atom to form a 1-alkene. When two free radicals interact, as in step (2), disproportionation occurs, with *n*-alkanes and 1-alkenes as the products. The alkyl free radical may also abstract a hydrogen atom from a neighbouring molecule, as in step (3), to form a *n*-alkane and a new free radical. Finally, longer chain *n*-alkyl free radicals tend, at higher temperatures, to decompose into ethylene and a shorter-chain free radical, as in step (4).

The net effect of the above four reactions is to produce a wide range of lower molecular weight alkanes and alkenes, when the bitumen is heated. This results in a lowering of the overall viscosity of the bitumen, which is normally termed "thermal visbreaking" in the petroleum industry.

The benzylic free radicals formed when alkyl sidechains are thermally cleaved from aromatic cores, as illustrated above, find it more difficult to abstract hydrogen atoms, because of their weaker benzylic bond. These radicals will primarily tend to combine with each other to build up larger ring systems. This type of reaction tends to increase molecular weight and is termed a condensation reaction:



The product of the above reaction converts readily, by oxidation, to the important tri-aromatic, anthracene, $C_{14}H_{10}$, which was first isolated from coal tar in 1832. By free radical reactions such as those illustrated above, all of which are known to occur from studies of the thermal decompositions of pure compounds, the types of products obtained in the thermal upgrading of bitumens can be very reasonably explained.

When upgrading is carried out in the presence of high pressures of hydrogen, and a catalyst which promotes hydrogen atom formation, the free radicals undergo fewer condensation reactions, since free hydrogen atoms are available to satisfy their need to form stable molecules:

$$R\bullet + H\bullet \longrightarrow RH$$

The net result of this type of reaction is a product of lower mean molecular weight than in simple thermal upgrading, and with a higher atomic H/C ratio. In addition, the fraction of very high molecular weight residues, with low H/C ratios, is reduced. This type of process, usually referred to as "hydrovisbreaking," will, in general, represent a more efficient utilization of the bitumen, and yield products with higher energy values.

From this brief discussion of the types of chemical reactions occurring during upgrading, it can be seen that we are gradually acquiring a more detailed understanding of the specific chemical mechanisms operative during these important commercial processes. As our knowledge increases, we will be able to design specific upgrading sequences which improve the yields of products of higher commercial value, and reduce the residues which often represent environmentally-undesirable by-products of commercial upgrading processes.

SUMMARY AND CONCLUSIONS

In this chapter an attempt has been made to outline briefly what is currently known about the myriads of chemical compounds present in the tarry natural substance known as bitumen. It will be apparent from the foregoing that the majority of the data we have on the specific composition of the bitumens are either semiquantitative or qualitative in nature. This is partially true because we do not yet know all of the compounds present in this complex material. Furthermore, of course, the compositional nature of bitumens varies with their location and their geochemical history.

Let us attempt to improve the mnemonic value of this short discussion of a complicated topic by attempting to summarize what we know quantitatively about the bitumens in terms of their chemical components.

Dealing first with those groups of compounds which are almost entirely hydrocarbons in nature, bitumens contain roughly 15 wt% of saturated hydrocarbons composed of one- to six-member rings, many of which are true terpenes. We can add to our hydrocarbon total, roughly 10 wt% of monoaromatics and another 9 wt% of di- and tri-aromatics, with the tri-aromatics partially contaminated with thiophenes. Thus we can say that approximately 34 wt% of bitumen is known to consist of hydrocarbons covering a wide range of structures and molecular weights.

The remaining two-thirds of bitumen embraces a vast array of compounds, including those containing the heteroatoms, sulphur, oxygen, and nitrogen. Sulphur is a particularly important element in the complex asphaltene structures. There it makes up about 7.6 wt% of the asphaltene, and is present both in thiophenic molecules, as well as in saturated rings.

Many of the homologous series involving heteroatoms have been characterized, but only qualitatively. The exceptions would be the carboxylic acids, which are terpenoid and hopanoid types, and amount to about 1–2 wt% of bitumen, and the cyclic terpenoid sulphides which account for from 6–14 wt% of the bitumen.

Among the series known only qualitatively are oxygen-containing fluorenones and fluorenols; some terpenoid sulphoxides, which are usually a relatively minor series produced by oxidation of the sulphides; and finally nitrogen-containing compounds such as the carbazoles, the quinolines, and some pyridines.

The small amounts of nickel and vanadium can, of course, be quantitatively estimated; these elements are partly associated with porphyrins in the asphaltenes and partly with other organic molecules which have not yet been firmly identified. Many more compounds remain to be structurally established, especially in this larger fraction of the bitumen. What is most important is that progress is being made at an increasingly rapid rate in both the identification and the quantitative estimation of the enormous number of chemical species in this highly complex natural mixture.

Thus we are gradually learning not only the identity of the compounds in bitumen, but

how they can be separated out as pure substances. Once chemists have pure samples of the compounds, they can study how fast they decompose, and the products of their decomposition. Furthermore, we can now relate the behaviour of the larger molecules in bitumen to simpler ones that have been studied in detail in the laboratory. As a result, we are now able to explain quite plausibly the types of products that are formed in the various upgrading processes currently in commercial operation.

Inevitably as chemical science progresses, we will be in a position to make an increasingly intelligent use of the chemical riches which nature has provided us, in such abundance, in the bitumens.

The Commercial Upgrading of Bitumen

As discussed in the preceding chapter, bitumen has a number of properties which set it apart from conventional crude oils. Thus bitumen contains approximately 17% of asphaltenes, and roughly one-half of the bitumen has a boiling point exceeding 524°C. In addition, bitumen is hydrogen-deficient, with appreciable concentrations of sulphur and nitrogen, as well as nickel and vanadium. And finally, its very high viscosity clearly distinguishes it from crude oils in general.

These properties define the extent of processing to which bitumen has to be subjected in order to be transformed into consumer products. From a chemical point of view, the upgrading and subsequent refining of bitumen into finished consumer products are, in fact, a continuum. In principle, the entire upgrading process could be carried out at a location remote from the mining and extraction site, provided that the viscosity of the bitumen is reduced sufficiently (by addition of diluent, for example) to make it suitable for transporting by pipeline. Alternately, the entire process, including the refining to consumer products, could take place directly at the site of mining.

The upgrading strategies selected for both the Syncrude and Suncor plants combine elements of these two options. At the oil sands plants, bitumen is upgraded into synthetic crude oil. The synthetic crude oil is then shipped by pipeline to refineries for further refining and blending into end-use consumer products.

This chapter focuses on the steps required to upgrade bitumen into synthetic crude oil. However, it is not the intent to provide an encompassing discussion of all upgrading processes and their variations. The emphasis will rather be on the basic chemical processes occurring in upgrading, illustrated by a few examples of typical upgrading sequences. In keeping with the aim of this chapter, some aspects related to the refining of synthetic crude oil into consumer products will also be discussed.

During the upgrading process, the following objectives concerning the composition and properties of the upgraded material are addressed:

1. Decrease of the metals (Ni, V) content.
2. Decrease of the mineral matter content.
3. Decrease of the sulphur and nitrogen content.
4. Increase of the hydrogen content relative to the carbon content.
5. Conversion of asphaltenes
6. Modification of the boiling point distribution (essentially this means conversion of the higher boiling materials into lighter fractions).

Typically, the upgrading process is carried out in two steps. Primary upgrading focuses on the conversion of pitch into lighter materials, on the adjustment of the hydrogen/carbon ratio, and on the removal of impurities and contaminants, such as metals and mineral matter. Nitrogen and sulphur are also removed to some extent.

During secondary upgrading, the products from primary upgrading are further treated to make them suitable as refinery feedstocks. The main objective here is to remove heteroatoms (sulphur, nitrogen, and oxygen) and to stabilize reactive groups, such as double bonds. Some aromatic saturation and hydrocracking also occur.

PRIMARY UPGRADING

Primary upgrading processes are frequently classified as either carbon-rejection or hydrogen-addition processes. In a carbon-rejection process, some of the feed is transformed into a carbon-rich stream which is then removed. In a hydrogen-addition process, as the name indicates, hydrogen is added to the feed through chemical reactions, with the objective of achieving conversion with little or no coke production.

The removal of coke, or carbon is typically achieved by thermal cracking at varying, but usually fairly severe conditions. A number of technical process variations for thermal cracking exist. Their common characteristic is that the feedstock disproportionates into a relatively low or even negative value carbon-rich stream and into a product stream.

Depending on the actual process selected, the carbon-rich stream can be either a heavy pitch or a solid coke. In both commercial plants operating in the Athabasca region, coke is produced, although different coking technologies are used in the two plants.

The basis of today's coking processes is the continuous thermal cracking process patented by Dubbs in 1913.[1] In this process, oil was thermally cracked into lighter material and into a heavier stream which was withdrawn from the bottom of the reactor. After becoming more familiar with their equipment, operators found that the distillate yield could be significantly increased by operating the reactor at a higher temperature and by closing the residuum valve. This allowed a more complete cracking reaction to occur. The coke formed under these conditions eventually filled up the drum which had to be shut down and cleaned out. In the 1930's, a second vessel was added, thereby permitting a continuous operation of this batch process by switching the reactors.

The modern delayed coker[2–4] operates on the same general principle. Delayed Coking is the process implemented at the Suncor plant.

Fluid coking[5,6] is a continuous process with continuous removal of coke from the process unit. This unit consists of two main vessels, the reactor and the burner. Flexicoking is an extension of the Fluid Coking process. A third vessel, the gasifier, is added in which essentially all the coke is gasified. In both processes, the vessels and connecting transfer lines are fluidized. Fluid Coking is the coking process implemented at the Syncrude plant. A schematic for the Fluid Coking Process is shown in Figure 1.

The coke-forming potential of a feed is often expressed as its MicroCarbon Residue (MCR) or its Conradson Carbon Residue (CCR) value. Both tests are functionally identical, i.e., destructive distillations. It is generally accepted that the more recently developed MCR test is less operator-dependent than the original CCR test. In these procedures, a sample of the feed is subjected to a specified heat-soak cycle. The amount of residue (coke) is then measured and expressed as a percentage of the feed. This is used, together with process-specific and proprietary information, to predict the coke-make in commercial coking units. A correlation between coke-make in a bench scale delayed type coker[7,8] versus the MCR value is shown in Figure 2. As can be seen, a linear (1:1) correlation was observed.

In the processes described above, the carbon-rich stream is coke, a solid carbonaceous material. In less severe thermal processes, a pitch rather than coke is produced. One example is the visbreaking process.[9–13] This process is also directly derived from the original Dubbs thermal cracking unit described above. Two different modifications have been developed: the soaker visbreaker, as shown in Figure 3, and the furnace (or coil)

1 F. Stoffa, Hydrocarbon Processing, May (1980) p. 101.
2 N.P. Lieberman, Oil and Gas Journal, Dec. 15 (1980) p. 71 and Dec. 22 (1980) p. 82.
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4 J.D. Elliott, "Modern Delayed Coking: Design and Operating Considerations for Maximum Liquid Yields," 1990 NPRA Annual Meeting, San Antonio, Texas, March 25–27 (1990).
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6 D.E. Allan, W.J. Metrailer, R.C. King, and S. Weichert, "Advances in Fluid and Flexicoking Technology," CEP, December (1981) pp. 40–44.
7 R.P. Kirchen, E.C. Sanford, M.R. Gray, and Z.M. George, "Coking of Athabasca Bitumen-Derived Feedstocks," AOSTRA Journal of Research, 5 (1989) p. 225.
8 R. Kirchen and E. Sanford, unpublished data.
9 L.M. Hus, Oil and Gas Journal, April 13 (1981) p. 109.
10 M. Notarbartolo, C. Menegazzo, and J. Kukh, Hydrocarbon Processing, Sept. (1979) p. 114.
11 R. Hoiurnac, J. Kuhn, and M. Notarbartolo, Hydrocarbon Processing, Dec. (1979) p. 97.
12 A. Rhoe and C. de Blignieres, Hydrocarbon Processing, Jan. (1979) p. 131.
13 M. Akbar and H. Geleen, Hydrocarbon Processing, May (1981) p. 81.

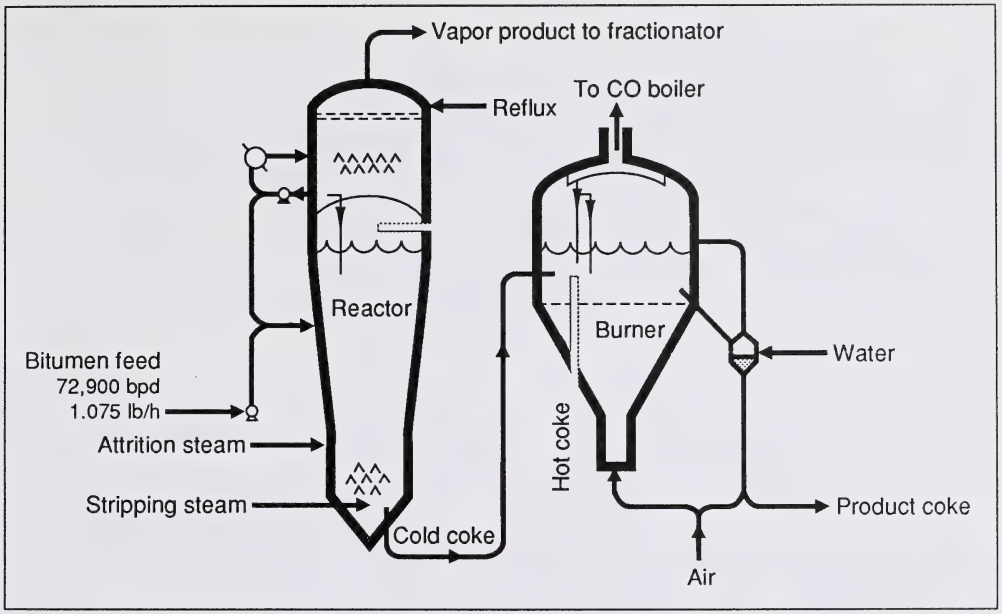

Figure 1. The Fluid Coking Process (reprinted with permission from: "Energy Heritage," Alberta Energy and Natural Resources, Edmonton, Alberta, Canada, p. 44).

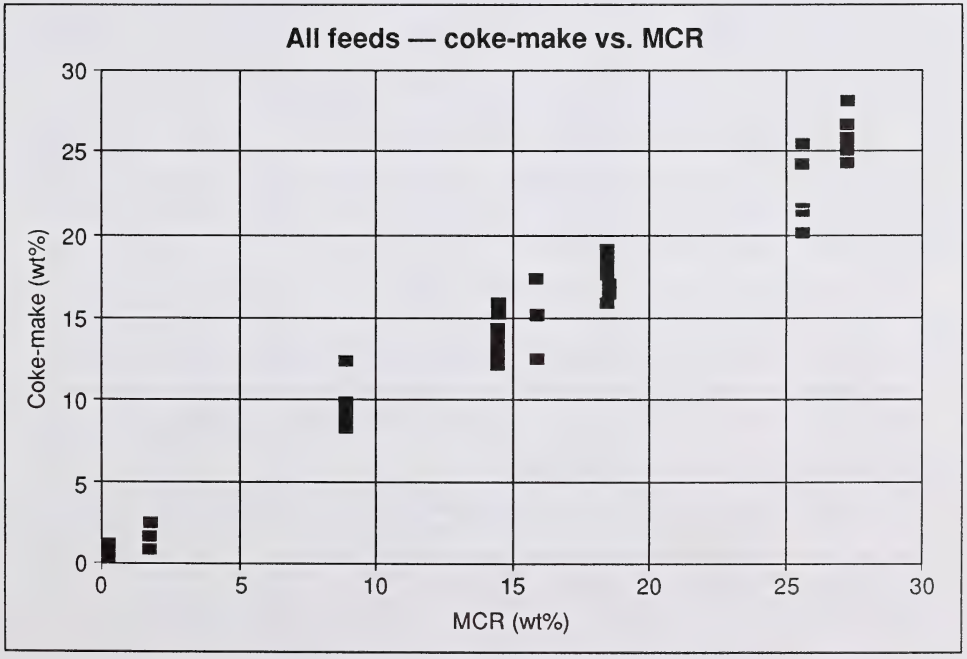

Figure 2. The relation between coke-make and MCR.

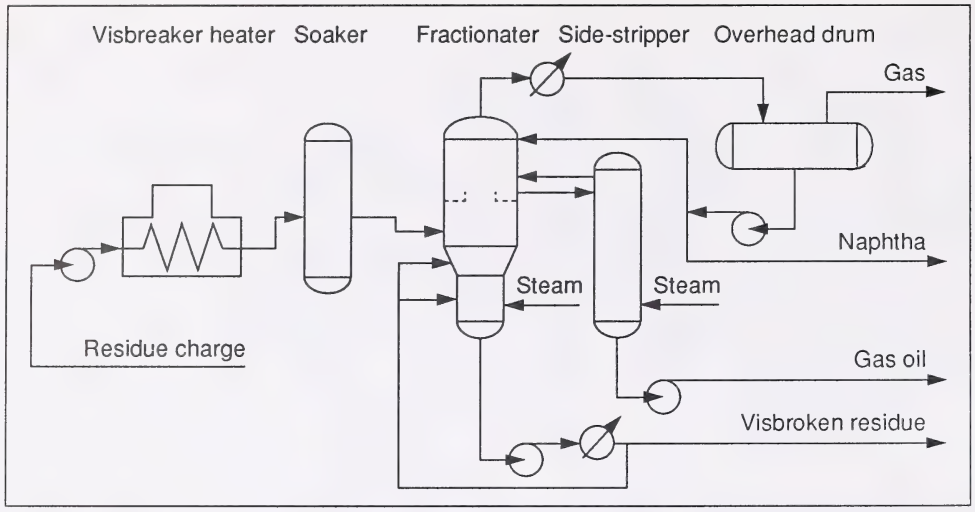

Figure 3. The Shell soaker visbreaker, simplified process scheme (reprinted with permission from: L.M. Hus, Oil and Gas Journal, April 13, 1981, p. 109, and ABB Lummus Crest, B.V., The Netherlands).

visbreaker in which the soaking drum has been eliminated. In this unit all of the cracking takes place in the coil, therefore, it usually operates at a higher temperature than the soaker visbreaker.

A more recent advancement in the thermal cracking process has been jointly developed by Kureha Industrial Company Ltd. and Chiyoda Chemical Engineering and Construction Company Ltd.[14,15] This Eureka Process, which is described later in this chapter, had been originally designed for the production of metallurgical coke. More recently, however, attention has been focussed on its capability to convert heavy residue into cracked oil.

Chemically speaking, thermal upgrading processes proceed via homolytic bond cleavage and free radical formation. The resulting free radicals then react in a complex network of chemical interactions including rearrangement, disproportionation, dehydrogenation, beta-scission, hydrogen abstraction, as well as reactions with other free radicals. Those interested in pursuing this subject in more detail should review the preceding chapter on "The Chemical Nature of the Alberta Bitumens."

The analytical technique of structural group analysis has been applied to products from bench-coking experiments.[16,17] Prior to the structural group analysis, the asphaltenes were precipitated by an excess of *n*-pentane. The supernatant liquid after distilling off the *n*-pentane, was then separated by chromatography into saturate, aromatic, and resin fractions. Class separation of the products showed less distinct differences than the feedstocks from which they were derived. This is not unexpected considering the severity of the thermal cracking reactions. These investigations yielded some extremely interesting results which merit a detailed study of the original papers.

As indicated above, asphaltenes are empirically defined as that fraction insoluble in a paraffinic solvent. In the laboratory, either *n*-pentane or *n*-hexane is used. As discussed in

14 T. Aiba, H. Kaji, T. Suzuki, and T. Wakamatsu, CEP, Feb. (1981) p. 37.

15 Y. Hirotany, T. Takeuchi, Y. Miyabushi, T. Aiba, and M. Shigeta, "Symposium on Residuum Upgrading and Coking," American Chemical Society, Division of Petroleum Chemistry, Atlanta, Georgia, March 29–April 3 (1981).

16 M.R. Gray, J.H.K. Choi, N.O. Egiobor, R.P. Kirchen, and E.C. Sanford, "Structural Group Analysis of Residues from Athabasca Bitumen," Fuel Science and Technology International, 7 (5–6) (1989) pp. 599–610.

17 M.L. Selucky, Y. Chu, T.C.S. Ruo, and O.P. Strausz, "Chemical Composition of Athabasca Bitumen," Fuel, 56, (1977), p. 369.

the previous chapter, asphaltenes consist of a dry, brownish powder. The coke-make from asphaltenes is very high, approximately 50 wt% for the Athabasca asphaltenes.

Several commercial processes for asphaltene removal are based on that same solubility property vis-a-vis paraffinic solvents; although the actual implementation of these processes shows distinct technical differences. For example, in the ROSE (Residuum Oil Supercritical Extraction) process, the solvent is recovered under supercritical conditions, rather than by conventional evaporation. This results in a significant utilities savings.[18]

Considering the low H/C ratio of the asphaltene fraction and the high coke-make from this fraction, an asphaltene precipitation process could be viewed as "carbon rejection." However, although the resulting de-asphaltened oil is now easier to upgrade, the asphaltene-rich fraction still contains potential products, and therefore must be utilized in an economically-attractive and environmentally-acceptable manner.

HYDROPROCESSING

During hydrogen-addition processes, hydrogen under pressure is chemically reacted with the feedstock. The reactions occurring include hydrocracking, hydrodesulphurization, hydrodenitrogenation, and the removal of metals. A major overall result of this treatment is that heavier components are converted into lighter materials. Typically, these processes are carried out in the presence of a catalyst.

In addition to reactions directly involving hydrogen, there are also thermal reactions occurring during hydroprocessing. This is because the temperature is in the range where such thermal reactions can take place, irrespective of the presence of hydrogen gas. The free radicals resulting from these thermal reactions are then quenched by various reactions with hydrogen. For example, it has been shown[19] that the conversion of high boiling material is primarily a thermal process, whereas the destruction of Conradson Carbon Residue (CCR) material involves catalytic processes.

Overall, hydroprocessing treatment shows a yield advantage when compared to thermal processes. This is primarily due to the fact that there is no large stream of low-value material, such as coke; in short a much larger fraction of the original feed is converted into a more commercially valuable liquid product.

Hydroprocessing technology is, in general, a more recent development than thermal upgrading technology. This is particularly true for feedstocks such as heavy oils and bitumens.

Trickle-bed hydroprocessing technology, which is typically used to hydrotreat distillates, and for which a large body of commercial experience exists, is sensitive to the presence of particulates in the feed. Accumulation of particulates in the catalyst bed leads to the build-up of a pressure-drop across the catalyst bed.

Fluidized or ebullated bed processes are more resistant to the presence of particulates in the feed. In this case, the catalyst is being maintained in a state of fluidization by the appropriate upward velocity of the liquid/gas phase. In practice, this is usually done by recirculating the liquid in order to obtain an adequate residence time. The commercial implementations of this approach are the LC-Finer Process and the H-Oil Process to be described later in this chapter.

An LC-Finer unit was started up at the Syncrude Plant in the Summer of 1988. The feed to the unit was raw bitumen, with a current design feed rate of 6400 cubic metres per day (40,000 bpd). The present unit is designed to operate in a relatively low conversion range. Accordingly, there is a significant stream of unconverted residue. This situation is perhaps distinct from what would occur in a grass-roots oil sands plant (with no existing cokers) where a higher conversion in the hydroprocessing unit might be preferable in order to minimize the residue stream.

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18 J. Gearhart and L. Garwin, "ROSE Process Improves Resid Feed," Hydrocarbon Processing, May (1976) p. 125.
19 E. Sanford, unpublished data.

In the LC-Finer process, a supported catalyst is used. Typically this is Co-Mo on alumina. The pelletized catalyst is maintained in a fluidized state in the reactor, and none, or very little of it, leaves the reactor by entrainment with the product stream. To counteract catalyst de-activation, some catalyst is periodically removed and replaced with fresh catalyst. Another approach is to use a catalyst of a much smaller size, which then leaves the reactor with the product. Owing to the much shorter time that a catalyst of this type is actually in use, it must show advantages either from a cost or activity point of view. Frequently this type of catalyst is referred to as a slurry catalyst or simply as an additive.

In the 1930's and 1940's, coal liquefaction plants were operated in Germany using an iron oxide-based additive. Hydrogen partial pressures were much higher than in today's processes — in the range of 7000–10,000 psi (49,000–69,000 kPa). This general technology was the basis for the development of the modern VEBA-COMBI-Cracking Process (VCC) to be discussed later in this chapter.

Another process based on additive systems is the CANMET Process.[20] This process, which is also described later, uses a mildly active additive, rather than a highly active catalyst. The additive performs a dual role: it inhibits coke formation during normal operation and it prevents severe coking under upset conditions. This Canadian process has been successfully operated at the 5000 bpd scale (800 cubic metres per day scale) at the CANMET Montreal Demonstration Plant.

SECONDARY UPGRADING

The liquid products obtained after primary upgrading still require further processing to transform them into a synthetic crude oil (SCO), which can then be refined into consumer products. Double bond compounds present in the products from primary upgrading are unstable and tend to react by forming gums and other heavy materials. Also the heteroatom content (i.e., N, S, and O) needs to be reduced to make a suitable refinery feedstock. Some heteroatom compounds also promote gum formation, as noted in the preceding chapter.

These required chemical changes are achieved by catalytic hydroprocessing. Typically, the products from the primary upgrading are fractionated, according to boiling range, into two or more streams. These streams are then hydrotreated individually according to the specifications for each stream. For example, the nitrogen specifications for the naphtha stream (which eventually becomes part of the gasoline pool) are much more stringent than those for the gas oil stream.

Catalytic hydrotreating is usually carried out in a trickle-bed reactor. This type of technology is available from a number of licensors. In this discussion, only generic trickle-bed process information is used. Thus typically, Ni-Mo or Co-Mo catalysts supported on alumina are employed. Ni-Mo catalysts generally show a higher activity for hydrodenitrogenation (HDN). In some cases Ni-W catalysts have been used for hydrotreating.

Representative hydrotreating catalysts consist of cylindrical, or multi-lobal extrudates; with catalyst diameters ranging from about 1/20 to 1/8 of an inch. The catalyst is loaded into the reactor, usually in several beds, separated by empty spaces.

At this stage the catalyst is still in the oxidic form (unless a commercially presulphided catalyst is used). To reach its optimum activity, the catalyst is then pre-sulphided under carefully controlled conditions. The reactor is now ready to be put into service.

As previously noted, the various streams are usually hydrotreated individually. This is because of the widely different specifications which these streams must meet.

For example, the IPL (InterProvincial Pipeline) specifications for naphtha from Athabasca bitumen is about 1 ppm of nitrogen. To prevent the double-bond compounds from polymerizing and forming gums in the reactor, relative mild conditions are used at the inlet to saturate the double bonds. This treatment is often done in a separate di-olefin reactor.

[20] D.J. Patmore, C.P.Khulbe, and K. Belinko, "Residuum and Heavy Oil Upgrading with the CANMET Hydrocracking Process," American Chemical Society, Atlanta Meeting (1981), Proceedings, p. 431.

Removal of heteroatoms, as the corresponding hydrogen compounds (H_2S, NH_3, and H_2O) are exothermic reactions. Hence there is a temperature gradient along the direction of flow of the feed, i.e., from top to bottom. This in turn drives the reactions faster. Provision is therefore made for the injection of quench hydrogen to control the reaction temperature.

The kinetics of hydrotreating a chemically-complex stream, such as coker gas oil for example, are defined by the reactivities and concentrations of the individual components. Experimentally, the kinetics are measured in pilot units, by determining the extent of reaction (i.e., sulphur removal or nitrogen removal) at various temperatures and at several reaction times.

One complication arises from the fact that only the total concentration of sulphur (or nitrogen) is known. It is the variation of this sulphur concentration as a function of time and temperature that is used to calculate the overall reaction kinetics. This, of course, assumes that all sulphur compounds present show exactly the same reactivity, and that they behave as one single compound. However, this is not in fact the case. The degree of sulphur removal is determined by the reactivities and concentrations of all the sulphur compounds. This situation is handled in practice by using empirically-developed equations.

In the remaining sections of this chapter, brief process descriptions will be given of the major primary upgrading methods of importance for bitumen treatment.

IMPORTANT COMMERCIAL BITUMEN UPGRADING PROCESSES

1. Delayed Coking

In the delayed coking process, the preheated feedstock is introduced into the lower part of the fractionator as shown in Figure 4. Here it contacts the hot vapours from the coking drum and

1: cools these vapours, thereby preventing coke formation in the separator;

2: causes the charge to be further pre-heated;

3: lighter (than the desired coker feed) material is distilled off.

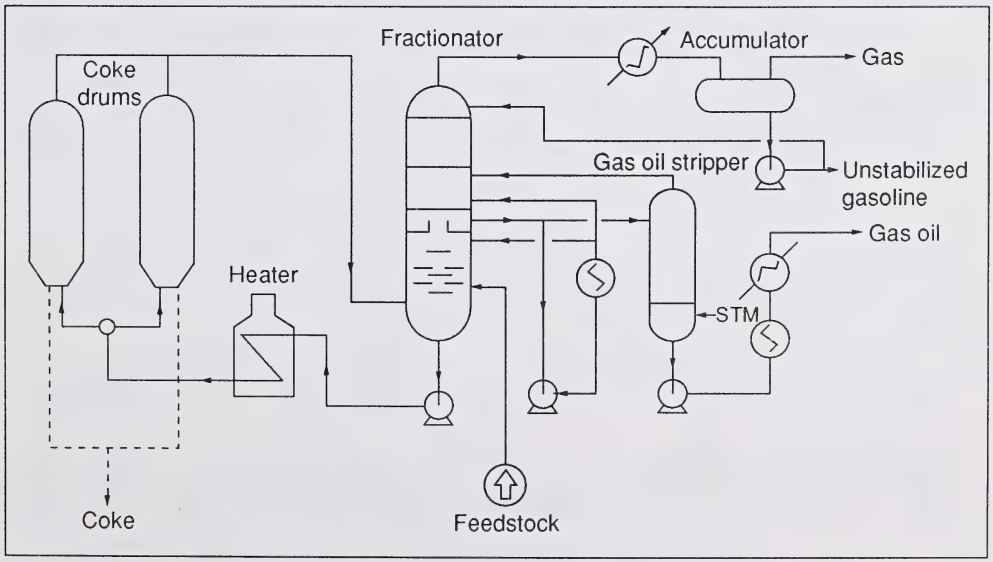

Figure 4. Delayed coking process flow diagram (reprinted with permission from "Heavy Oil Processing Handbook." The Chemical Daily Company, Figure 1, p. 18).

The remaining feed is then combined with recycle material from the condenser and fed, via the coker heater, into the active coker drum. Steam is added, to act as diluent and to control velocities and residence time. The feedstock stream is "atomized" and the high temperature, in combination with an appropriate residence time, causes part of the material to form coke. This coke deposits in the drum.

The vapours, consisting mostly of product hydrocarbons, steam, and hydrogen sulphide, exit the coker drum. These vapours are then fed into the fractionator section, where they are separated according to their boiling points. They are then sent to downstream units.

When the active coke drum is filled to the desired level, the feed leaving the heater is directed to the other drum. The filled drum is then steam-stripped to remove residual hydrocarbons and is cooled with water. The cold drum is opened and the coke is removed in a process using high pressure water jet cutting. The empty drum is then closed, purged with steam, and pre-heated. It is now ready for a new coking cycle.

2. Fluid Coking and Flexicoking

Fluid coking[21,22] is a continuous process with continuous removal of coke from the process unit. The process unit consists of two vessels, the reactor and the burner. Flexicoking is an extension of the fluid coking process. A third vessel, the gasifier, is added, in which essentially all the coke is gasified. In both processes, the vessels and connecting transfer lines are fluidized. A complete process flow diagram is shown in Figure 5.

The pre-heated feed, consisting of fresh feed and recycle, is injected through multiple nozzles into a fluidized bed of hot coke particles (typical: 480 to 540°C). Steam is used as fluidizing agent. The feed is "atomized" and deposits on the coke particles, which provide a large surface area. The feed is cracked into lighter products. During this process a new growth ring of coke is formed on the individual coke particles.

The volatile reaction products leave the reactor through cyclones which remove most of the entrained coke particles and return them to the reactor. Products vapours are then sent to the scrubber section, which is mounted directly above the reactor. Unconverted feed is condensed and coke dust is scrubbed out of the products. The resulting slurry is recycled to the reactor.

Product vapours are then sent to a conventional fractionator and separated according to their boiling point, after which they are directed to downstream units for further processing.

In the lower section of the reactor vessel, coke particles are steam-stripped to remove residual hydrocarbons. Larger coke particles are attrited through injection of steam. Coke is then withdrawn from the reactor vessel and transferred into the burner vessel. The transfer line is also fluidized by steam. Air is injected into the burner (typical: 595 to 650°C) and a sufficient quantity of coke is burned to satisfy the heat requirements of the process. The hot coke is then transferred from the burner to the top of the reactor vessel, to start a new cycle.

Coke produced that is in excess of the amount required for satisfying the heat requirements is sized via the elutriator: finer coke particles are returned to the process, coarser particles are quenched with water and withdrawn. Control of particle size is also carried out here.

Combustion products from the burner pass through two stages of cyclones where entrained solids are removed. Typically, combustion gases are burned in CO boilers to raise steam.

The reactor and coke transfer lines of the flexicoking process are similar to those of the fluid coking process. The burner is replaced with a heater and, as indicated above, a third vessel — the gasifier — is added. Excess coke is transferred from the heater to the gasifier

[21] S.F. Massenzio, "Exxon Fluid Coking and Flexicoking Processes for Synfuels Upgrading Applications," in R.A. Meyers, "Handbook of Synfuels Technology," McGraw-Hill, New York (1984).

[22] D.E. Allan, W.J. Metrailer, R.C. King, and S.W. Echert, "Advances in Fluid and Flexicoking Technology," CEP, Dec. (1981) p. 40–44.

rather than being removed from the process unit. In the gasifier, the coke is reacted with air and steam.

$$C + H_2O \longrightarrow CO + H_2$$
$$H_2O + CO \longrightarrow CO_2 + H_2$$

This gas typically passes through a sulphur recovery unit and is then used for heat generation.

3. Eureka Process

The flow diagram of the Eureka process (Figure 6) shows some similarity with that of the delayed coking process, however:

1: the feed is not injected at the base of the reactor, but in the central part; steam is injected at the bottom;

2: reactor switching is carried out more frequently (i.e., every two hours);

3: the residue is a liquid pitch under reactor conditions.

The feedstock is pre-heated to about 340°C and enters the fractionator where it is mixed with recycle material. It is then pumped to the heater and heated to about 500°C. This hot material is fed into the reactor, and superheated steam is injected at the base of the reactor.

The reaction products, together with the steam, are directed to the fractionator. Entrained pitch is separated and recycled to the reactor.

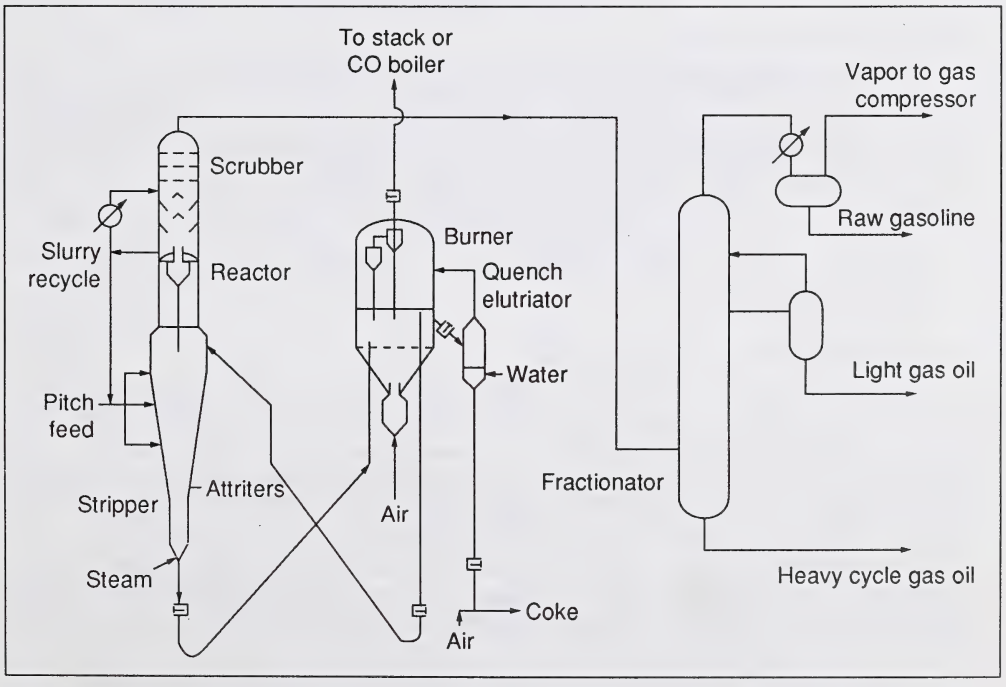

Figure 5. Fluid coking process flow diagram (reprinted with permission from "Heavy Oil Processing Handbook." The Chemical Daily Company, Figure 1, p. 20).

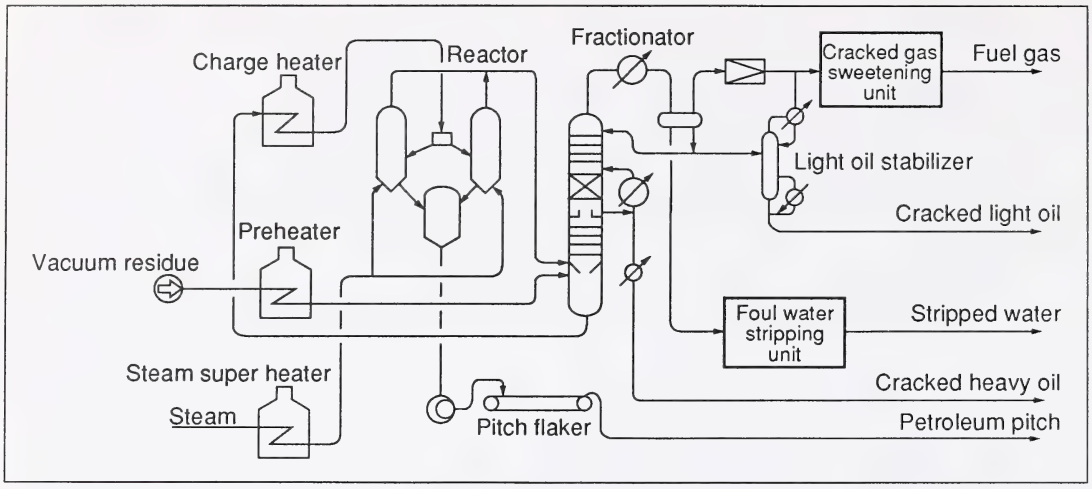

Figure 6. Eureka process flow diagram (reprinted with permission from "Heavy Oil Processing Handbook." The Chemical Daily Company, Figure 1, p. 12).

The viscosity of the reactor bottom material increases due to polycondensation reactions. When the viscosity reaches the desired value, this material is quenched and drawn off into the stabilizer vessel. At the same time, the feed is switched to the second vessel. This hot pitch is pumped from the stabilizer to the pitch flaker, where it solidifies as it is cooled off.

4. The LC-Fining: Process

In the LC-Fining Process, hydrocarbon feed and hydrogen enter at the bottom of the reactor[23] as illustrated in the process flow diagram in Figure 7. The reactor is of the ebullated type; i.e., liquid from the top of the reactor is recirculated to the bottom of the reactor to maintain the reactor catalyst bed in an expanded or ebullated state. This type of reactor is largely isothermal, as the heat of reaction is dissipated and spread to the entire reactor volume. Catalyst is withdrawn periodically and replaced with fresh catalyst. Hence, after some time of operation, catalyst composition reaches a constant, or equilibrium state.

Depending on the particular application, two or, as shown in Figure 7, three reactors may be used in series.

5. The VEBA-COMBI-Cracking Process

The flow diagram for this process (Figure 8) can best be described as consisting of two distinct, though integrated, sections: the liquid phase reactor and the gas phase reactor.

Feedstock, such as heavy crude or residue, is mixed with the proprietary additive. After hydrogen addition, the feed flows into the liquid phase reactor, where hydrogenation reactions occur. Typical conditions are 440 to 485°C and 150 to 250 bar (15,000–25,000 kPa).[24] The liquid phase reactors are fed in an upflow mode and have no internals.

The outflow of the liquid phase reactor is directed to a hot separator. Here, the non-converted feed and potential solids are separated and withdrawn from the unit. The overhead is directed to a hydrotreater. The function of this reactor is similar to a

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23 R.P. Van Driesen and L.L. Fornoff, "Upgrade Results with LC-Fining," Hydrocarbon Processing, Sept. (1985) p. 91. R.E. Boening, N.K. McDaniel, R.D. Peterson, and R.P. Van Driesen, Ibid. Sept. (1981) p. 59.

24 F.W. Wenzel, U. Graeser, and K. Niemann, "VEBA-COMBI-Cracking, A Proven Technology for High Conversion of Heavy Bottoms," Tar Sands Symposium, Proceedings (1986).

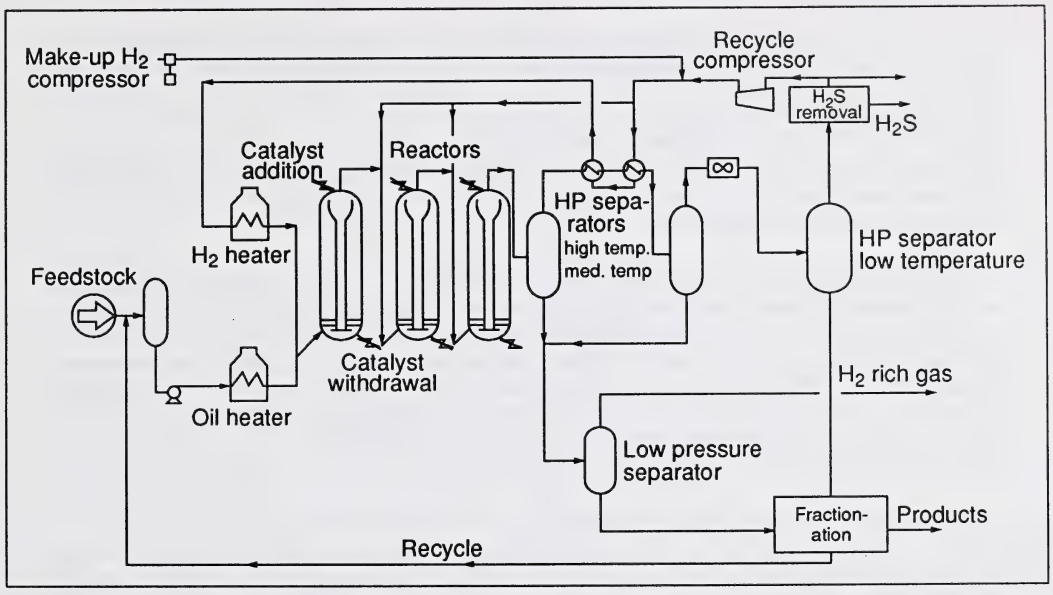

Figure 7. LC-fining process flow diagram (reprinted with permission from "Heavy Oil Processing Handbook." The Chemical Daily Company, Figure 1, p. 48).

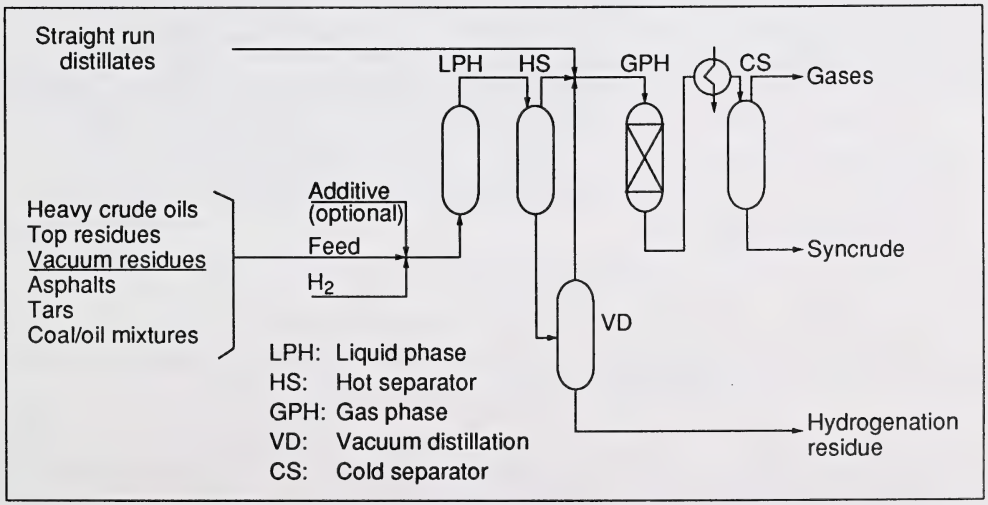

Figure 8. The VEBA-COMBI-Cracking flow diagram (reprinted with permission from F.W. Wenzel, U. Graeser, K. Niemann, "VEBA-COMBI-Cracking, a Proven Technology for High Conversion of Heavy Bottoms," Proceedings, Tar Sands Symposium, Jackson, Wyoming, July 7–10, 1986.

conventional hydrotreater. The reactor is operated in a trickle, downflow mode. The products from the gas phase reactor are sent to a cold separator, from which the synthetic crude is withdrawn.

One characteristic feature of this process is the direct coupling of the two reactors, i.e., the conversion step and the hydrotreating step.

The CANMET[25] Hydrocracking Process

This relatively new hydrocracking process uses a low-cost additive to inhibit coke formation and allow high conversion of the heavy feed to products of lower molecular weight and higher H/C ratio.

In the process, the feed, combined with the additive, is mixed with hydrogen and fed through heaters into the reactor, as illustrated in Figure 9. It should be noted that this mixture enters the vertical reactor at the bottom. The reactor operates as an upflow bubble column, in the temperature range, 820–850°C, and at about 2000 psi (14,000 kPa). Temperature measurements on the column show that it is functioning in an isothermal mode. The hydrogen and the hydrocarbons rise through the suspension of additive particles, which act to suppress coke formation, and remove metals such as nickel and vanadium, so that the distillate emerges substantially metals-free.

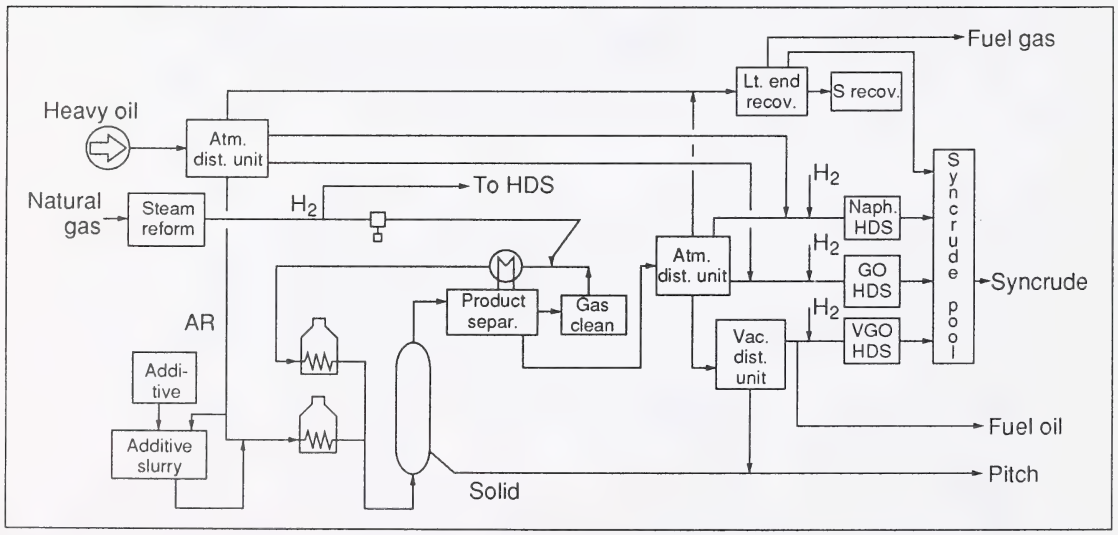

Figure 9. CANMET hydroprocessing flow diagram (reprinted with permission from "Heavy Oil Processing Handbook." The Chemical Daily Company, Figure 1, p. 56).

The reactor effluent is fractionated and the individual cuts are sent to the appropriate hydrotreaters. The additive remains with the pitch stream.

This concludes our discussion of the upgrading processes which are currently of commercial importance in converting Alberta bitumens into refinery feedstocks.

25 Derived from "Canada Centre for Mineral and Energy Technology."

Foreword to the Analytical Procedures

This second volume of analytical methods from Syncrude Canada Ltd. describes procedures that have been used for the support of research studies of bitumen upgrading processes. Readers should understand that not all research-generated methodologies are published here: only the most routinely and current-used procedures. The Analytical Services Section of Syncrude's Research Department has an on-going objective of developing the most efficient analytical technology that is available for industrial bitumen upgrading research. Particular methods are often selected because they fill, for example, a high productivity need, as is the case for nitrogen and sulphur determinations using the Antek method.

A study of these methods will reveal that quite often the preferred methods involve the use of microprocessor-aided data handling and process control hardware. Such are the cases for metal determinations by plasma, nitrogen, and sulphur by Antek equipment, density measurements with the Anton-Parr analyzer, microcarbon (MCR) assessments, and the automated distillation unit for performing ASTM D1160 testing, to mention a few examples. Much of this methodology is under constant study and subject to replacement, especially if better costs-per-determination can be achieved, and even more often, where advances in computer technology can improve both accuracy and precision, and frequently the time required per analysis.

Regarding the group of methods dealing with catalyst testing, Syncrude makes no claim to their originality. These methods were developed in close collaboration with our catalyst manufacturers, as well as by careful study of the open literature, and particularly the literature provided by fabricators of laboratory equipment. It should be noted that the description of each procedure specifically identifies the equipment that was selected and provides references to all literature utilized.

Pertinently, it must be emphasized that the task of keeping analytical technology up-to-date is an expensive business. Syncrude Research is making every effort to stay abreast of these advances in analytical research, and continues to invest major capital funds in analytical hardware. However, there is still need to do better. We recognize, for example, that our Bromine Number procedure is not yet modernized in terms of automated titration technology. However, the production demand for this type of improvement has not yet materialized.

Finally the points listed in the Preface regarding the use of these procedures should be noted carefully, especially those relating to safety requirements.

2

ELEMENTAL ANALYSIS

Determination of Carbon and Hydrogen in Hydrocarbon and Catalyst Samples

INTRODUCTION:

The measurement of the carbon and hydrogen content is an important indicator used to monitor Syncrude's upgrading process streams. The degree of cracking of bitumen and hydrogenation of the resulting gas oil streams can be estimated using the carbon-to-hydrogen ratio. Carbon and hydrogen analysis is also performed on spent hydrocracking catalyst to provide an indication of the degree of coke formation on the catalyst.

SCOPE:

1. This method determines the amount of carbon and hydrogen present in liquid and semi-liquid hydrocarbon samples.
2. This method can also determine the amount of carbon and hydrogen present in catalysts.

SUMMARY:

A weighed quantity of sample is placed into a small capsule with a combustion aid (Com-aid). This capsule is dropped into a ceramic crucible which sits in a U-shaped combustion tube. The sample is burned in oxygen at 950°C. The combustion products include CO_2 and H_2O which are constantly monitored during combustion by infrared detectors. When the combustion is complete, an aliquot is taken and the CO_2 and H_2O are measured by selected infrared detectors. These measurements are weight-compensated and displayed digitally as percent C and H.

BACKGROUND:

The analysis of carbon and hydrogen content of Syncrude process streams is an important part of their overall characterization and quality assurance.

There are a number of analysis instruments available, the majority of which are based on a controlled combustion of the sample and the measurement of the amount of carbon dioxide and water produced. Several techniques selectively trap the water and carbon dioxide on adsorbents and gravimetrically determine the C and H content. Other instruments measure through infrared absorption the amount of water or carbon dioxide present in a fixed volume of gas at a defined pressure. A version of the latter instrument was selected for our laboratory due to the robustness of the instrument operation and the sample size involved. The sample size is important in that some instrumental techniques require only several milligrams of sample. Owing to sample inhomogeneity, this is often not practical for a number of our sample types. The selected instrument will accept several hundred milligrams of samples.

SAFETY CONSIDERATIONS:

1. Compressed gases should be handled with care.
2. Handle the hot crucible and lance with care.

WASTE DISPOSAL:

1. Dispose of excess sample materials into a suitable hydrocarbon storage tank.
2. The crucible full of combusted samples, once cooled, can be disposed of in the appropriate waste container.

APPARATUS, REAGENTS, AND MATERIALS:

1. LECO CHN-600 Analyzer, LECO Corporation, St. Joseph, MI, USA Model 785-500.
2. LECO LB-80 Electronic Balance, Model 759-300.

3. ISOREG Computer Power Module, ISOREG Corporation, Littletown, MA, USA.
4. Oxygen: 99.995%, Matheson.
5. Paraffin Oil Standard, LECO Part #501-439.
6. Residual Fuel Oil Standard, LECO Part #502-083.
7. Sucrose Standard, LECO Part #501-441.
8. Standard Tin Capsules, LECO Part #501-059.
9. Large Tin Capsules, LECO Part #502-040.
10. Copper Capsules with tin plugs, LECO Part #501-571.
11. Com-aid for liquids, LECO Part #501-427.
12. Com-aid for solids, LECO Part #501-427.
13. Ceramic Crucibles, LECO Part #529-026.
14. Crucible Extraction Tool, LECO Part #776-285.
15. Sample Tweezers, LECO Part #502-028.

SAMPLE CONSIDERATIONS:

Amount Required: 1.0 g

Destructive: Yes

Properties: Homogeneous liquid and semi-liquid hydrocarbon samples.

Homogeneous catalyst samples.

PROCEDURES:

Instrument Parameters:

1.	Primary Furnace Setting	950°C
2.	Secondary Furnace Setting	950°C
3.	Calibration Stack Length	5
4.	Delta Carbon IR	200
5.	Delta Hydrogen IR	300
6.	Regulators for O_2 and N_2 @ 40 psi	
7.	Burn #1 Time	30 s
8.	Purge #6 Time	10 s

9. Change Crucible Interval
   - 40 samples in standard tin capsules
   - 25 samples in large tin capsules
   - 15 samples in copper capsule with tin plugs
   - These values may be changed depending on the sample type.
   - After changing the crucible a blank should be run.
10. Furnace Reagent Interval
    - 1000 samples
11. Oxygen Profile
    - Flow #7 for 20 s
    - Flow #4 for 20 s
    - Flow #3 until end

Start-up Procedures:

1. Ensure that sufficient gases are present. Push the gas key to turn on the oxygen.
2. Check the values of the system constants.
3. Check the ambient monitor.
4. Determine the system blanks by depressing the BLANK key. The message centre will display: CARBON BLANK 00.00 MOD BY KBD.
5. Push the ZERO key until all zeros are displayed, then push the ENTER key. Continue, similarly, for the hydrogen blank value. The message centre will now display: REPEAT BLANKS – YES/NO.
6. Push the YES key. The message centre will display: NO OF ANALYSIS 01 MOD BY KBD.
7. Enter the desired number of analysis (usually three), then push the ENTER key. The instrument will continue through the blank analyses. When the analyses are complete, manually average the blank results and enter by pushing the BLANK key. By responding NO to the REPEAT BLANKS message, the system will return to the idle loop.

Calibration:

1. Analyze five standard samples of the same material. Choose a standard most like the samples to be run.
2. Place the appropriate capsule on the balance. When the weight is stable, push the TARE key on the control console. Remove the capsule and add the Com-aid. Place the capsule with the Com-aid back on the balance and push the TARE key again. Load about 0.1 g of standard sample material into the capsule and crimp or plug the top. When the weight stabilizes, push the ENTER key. If using standard tin capsules, drop the capsule into the autoloader and push ANALYZE to advance the autoloader. The sample will drop into the loading head port and the analysis will proceed automatically. If the larger size capsules are used, they must be loaded individually into the loading head port.
3. If the AUTO/MANUAL switch is in the AUTO position, the next standard samples can be weighed and entered in a similar fashion, and the samples will be analyzed in an uninterrupted sequence with the results automatically printed after each analysis.
4. Once the standard samples have been analyzed, push the CAL key. The message centre will display: CALIBRATE BY BURNS – YES/NO.
5. Push the YES key. The message centre will display: DISPLAY AS DET ANSWERS?
6. Press the YES key to calibrate with the determined answers. The message centre will now display: CALIBRATE CARBON – YES/NO.
7. Push the YES key and a listing of the burn results will be printed. The message centre will display: CARBON STD % 088.76 MOD BY KBD.
8. Enter the standard sample's carbon content by pushing the appropriate number keys and ENTER. The message centre will present the results in the calibration stack one at a time. If the result is to be used to calibrate, press the YES key or NO to exclude the result. When all the desired results have been selected, the message centre will calculate the new calibration number and the carbon blank value, corrected for this new calibration, and the results will be printed. The message centre will display: CALIBRATE HYDROGEN – YES/NO.

9. Press the YES key and proceed in the same manner as for carbon. When complete, the answer stack will be printed with all the results corrected by the new calibration values. The system will then return to the idle loop .

Analysis of Samples:

1. The preliminary treatments of the various types of samples encountered are summarized in Table 1.
2. Samples are weighed and analyzed as outlined in the calibration procedure.
3. If an ID code is desired, press the ID CODE key prior to weighing the sample. The message centre will display: 0000000000 MOD BY KBD.
4. Press the number keys to display the desired number. Only the first eight digits can be set since the remaining two are the automatic counter.
5. A maximum of 30 ID codes and weights can be entered in the weight stack. Enter the ID code and sample weight in the order they are to be analyzed.
6. If the autoloader is to be used, rotate the carousel so that position 49 is over the drop tube and place the capsules into the carousel, beginning at position 1. Push the ANALYZE key to start the analysis. The CHN-600 will continue to analyze the samples in the carousel without operator attention.

Table 1. Treatment procedures for various sample types

Sample type	Standard type	Capsule type	Change crucible interval	Mass of Com-aid grams	Mass of sample grams	Special considerations
Naphtha	paraffin oil	copper capsule with tin plug	15	0.2–0.3	0.1	allow sample to soak into Com-aid before weighing and capping
LGO	paraffin oil	copper capsule with tin plug	15	0.15–0.2	0.1	allow sample to soak into Com–aid before weighing and capping
HGO	residual fuel oil	standard tin	40	0.1	0.1	none
Bitumen	residual fuel oil	large tin	25	0.1	0.1	warm in oven at 70°C for more than one hour
Coke slurry	residual fuel oil	large tin	25	0.1	0.1	chip off appropriate size subsample
Coke	sucrose	standard tin	35	0.1[1]	0.1	none
Catalyst	sucrose	standard tin	35	0.1[1]	0.1	sample should be shattered or ground into a fine dust

1 Com-aid for solids

7. If the autoloader is not used, the samples can still be entered into the weight stack; however, it is important to ensure that the next sample to be analyzed is loaded immediately following the previous sample drop. This can be eliminated by switching the AUTO/MANUAL switch to the MANUAL position. It will then wait after each analysis for the next sample to be loaded and the ANALYZE key to be pushed before proceeding.
8. After each analysis is complete, the results for carbon and hydrogen will be displayed and printed.
9. After the CHN-600 has been idle for more than half an hour, or any changes have been made, check the standard sample. If the deviation is greater than 0.30%, recalibrate the instrument.
10. Each sample should be analyzed in at least triplicate, with the median values reported.

Instrument Shutdown:

1. The furnace controls may be left at their normal settings. Push the gas key to turn off the oxygen flow.

CALCULATIONS:

1. No calculations need to be done. The CHN-600 calculates and prints the weight percent values for the sample.
2. Report the median percent carbon and hydrogen printed by the CHN-600 for replicate analysis.

REPORT FORMAT:

The carbon and hydrogen content is reported to the nearest 0.01%.

PRECISION AND ACCURACY:

- Precision evaluations of the repeatability of the carbon and hydrogen determinations have been carried out on three different sample types: light gas oils, heavy gas oils, and bitumen feeds. The results are given below.

Table 2. Average standard deviations for three sample types

	Average standard deviation		
	%C	%H	
Light gas oils	0.40	0.11	(n = 23)
Heavy gas oils	0.29	0.07	(n = 15)
Bitumen feeds	0.42	0.07	(n = 11)

- Accuracy is determined by comparison with reference standards purchased from LECO and NBS. These analyses are compared with the calibration standards during routine operation.

REFERENCES:

- LECO Corporation, "CHN-600 Elemental Analyzer for Macrosamples Septum 785-500," St. Joseph, MI, USA, 1987.

Metals in Hydrocarbon Analysis by ICAP-AES

INTRODUCTION: The bitumen upgrading feed and product streams are monitored for metals content for several purposes: (1) to track the degree of potential catalyst poisoning that may occur within the reactor due to feed metals content; (2) to monitor the degree of catalyst physical or chemical breakdown into the product streams; and (3) to provide one of many indicators of change in the process operation. The feed stream to the cracking units is dry bitumen containing solids in the <20 µm range. Solids content of the product streams, light gas oil to heavy residual fractions, are highly variable in both solids loading and particle size distribution.

SCOPE: This method determines the amount of Ni, V, Fe, Al, Co, Si, and Mo in a hydrocarbon matrix. The method was specifically developed for the analysis of feed and heavy oil products related to the Syncrude upgrading process.

SUMMARY: A 5-g sub-sample of the hydrocarbon is diluted to 100 g with 20 g of neutral base oil and xylene to weight. This solution is then directly aspirated into the Inductively Coupled Argon Plasma Emission (ICAP) Spectrometer. The emission intensities of the elements of interest are then compared with those of standard solutions of known concentrations, previously analyzed. Results are reported in terms of mg/kg of sample for each element.

BACKGROUND:

1. The analysis of process stream solids can be accomplished by several instrumental techniques: Inductively Coupled Argon Plasma (ICAP) Spectrometry, Atomic Absorption (AA) Spectrometry, and X-ray Fluorescence (XRF) Spectrometry. Each technique has limitations in terms of sample preparation, sensitivity, subsampling, time for analysis, and overall ease of use. AA provides very high sensitivity but requires careful subsampling, extensive sample preparation, and detailed sample-matrix corrections. XRF requires little in terms of sample preparation but suffers from low sensitivity and the application of major matrix corrections. The ICAP provides high sensitivity and few matrix corrections, but requires a considerable amount of sample preparation depending on the process stream to be analyzed. The ICAP was selected as the instrumental technique of analysis for Syncrude due to availability and sensitivity.
2. The ICAP is an instrument routinely used for the analysis of the dissolved metal composition of aqueous samples. Solid samples are prepared in such a way, ashing then fusion, that their final analysis matrix is in the aqueous dissolved form. The analysis of metals in a hydrocarbon matrix, potentially containing solids important to the analysis, is a problem. The ashing of a hydrocarbon sample containing metals, whether in organically-complexed, elemental, or inorganically-complexed form, can lead to analysis errors in that some of the complexes, specifically the organo-metallics, are in a volatile form at typical ashing temperatures (700–800°C). The organically-complexed metals tend to originate in the high molecular weight hydrocarbons found naturally in the feed or generated in the reactor. The inorganic metal complexes originate naturally in the feed, or from the breakdown of catalyst, or the formation of inorganic complexes under the reactor conditions. Without ashing and subsequent fusion, any solids present

tend to either clog the ICAP nebulizer or, due to their mass, not reach the analytical region of the ICAP plume. In either case an analysis error is introduced. The requirement for the analysis of metals around the hydrocracker pilot plant and commercial unit is an example of an analysis requiring the total concentrations of the various forms of the metals present.

3. The solution to this problem is to directly aspirate the hydrocarbon of interest into the plasma in such a way that the solids present are not eliminated from the analysis. This involves a change in configuration, notably the nebulizer, spray chamber, torch, analytical observation zone, and general operating procedures of the instrument in order to function with the hydrocarbon matrix and the presence of suspended solids.

SAFETY CONSIDERATIONS:

ICAP Spectrometer:

1. Avoid direct exposure to the high-intensity ultra-violet light produced by the plasma.
2. Caution is required when dealing with the ICAP instrumentation due to the very high power levels present.

Xylene:

1. Low level exposure: irritation of nose, throat, and eyes.
2. Refer to Materials Safety Data Sheet (MSDS) for details.

Feed and Product Process Streams:

Refer to MSDS information for safe handling procedures.

APPARATUS, REAGENTS, AND MATERIALS:

Inductively Coupled Argon Plasma Spectrometer
Applied Research Laboratories,
ICAP Model 3580,
Applied Research Laboratories,
Valencia, CA., USA

Peristaltic Pump
Gilson Minipuls Model MPl,
Gilson Medical Electronics Inc.,
West Beltine Highway,
Middleton, WI., USA

Porcelain Crucibles

Balance: capable of four significant figure accuracy.

Volumetric Flasks: 100, 250, 500 mL Class A.

Conostan Standards

Co: • 5000 wppm in hydrocarbon

S21: • 500 wppm in hydrocarbon
• 21 metals including Ni, V, Mo, Fe

Neutral base oil: viscosity 85
Conostan Division,
Conoco Inc.,
Ponca City, OK, USA

SAMPLE CONSIDERATIONS:

Amount Required: 25 g
Destructive Analysis: Yes

PROPERTIES:

Problems may occur if the solids loading is very high and/or if the particle size distribution of the solids indicates the presence of large (>50 μ) particulates. Problems will also occur if the hydrocarbon composition has a large fraction of highly volatile components or components that are not miscible with xylene. The viscosity of the sample must be maintained at a suitable value relative to the operation of the spray chamber and nebulizer. Adjustments to the amount of neutral base oil added during the sample and standard preparation should be made.

PROCEDURE:

Calibration:

Preparation of calibration standards

ORGBL (0 ppm)	10 g neutral base oil 85 90 g xylene to weight
ORGLO (10 ppm)	20 g neutral base oil 85, 4 g S-21 standard 4 g Co organic matrix standard 172 g xylene to weight
ORGHI (50 ppm)	10 g neutral oil 85 10 g S-21 standard 10 g Co organic matrix standard 70 g xylene to weight

Note:
- Co is not included in the S-21 organo-metallic standard.
- The standards are stored in glass bottles for a maximum of one week.
- Fresh standards are then required.

IMPLEMENTATION OF STANDARDS:

The calibration standards are aspirated into the ICAP AES system and stored as reference calibration curves for the samples of unknown composition.

SAMPLE ANALYSIS:

1. Transfer a 5-g portion of the hydrocarbon to be analyzed into the glass jar.
2. Transfer a 20-g portion of the neutral base oil into the glass jar.
3. Fill to 100 g with xylene. Replace lid.
4. Mix thoroughly through repeated inversions of the jar.
5. Set the plasma spectrometer to the following configuration:

Power	1200 watts
Reflected Power	<5 watts
Nebulizer	ARL V Groove MDSN
Nebulizer Pressure	30 psi
Spray Chamber	ARL Mini-chamber
Peristaltic Pump/ Nebulizer Feed Tubing	Viton 1.52 mm I.D.
Observation Height	15 mm above top coil
Coolant Gas Flow	12 L/min Ar
Plasma Gas Flow	0.8 L/min
Sample Gas Flow	0.5 L/min
Sample Uptake Rate	2.4 mL/min

6. Aspirate sample into ICAP-AES for analysis following the manufacturer's software procedures.
7. Monitor sample uptake rate to ensure nebulizer has not become plugged.
8. Aspirate blank after every third sample. This serves to prevent a sample accumulation in the spray chamber and/or nebulizer and the resulting memory effects.
9. Aspirate a standard sample at appropriate intervals, every three or four samples, to check system response over the analysis time frame.

CALCULATIONS:

1. The analysis results are to be reported in terms of mg/kg of the element Ni, V, Fe, Co, Mo, Si found in the sample.
2. The ICAP-AES computer system prints the results directly in terms of mg/kg, background corrected, relative to the calibration standards used.

REPORT FORMAT:

The results are reported in terms of mg/kg of metal present in the hydrocarbon sample.

PRECISION AND ACCURACY:

Precision:

Analysis results typically have a %RSD <5%. This is well within the requested precision for Syncrude upgrading samples.

Accuracy:

Results of analyses have been compared with the results of other subsample analyses performed at external laboratories. The accuracy was considered to be adequate for this application.

Simultaneous Determination of Nitrogen and Sulphur in Liquid Petroleum Hydrocarbons by Chemiluminescence and Fluorescence

SCOPE

This method determines the amount of chemically-bound nitrogen and the total sulphur content in liquid hydrocarbon samples.

SUMMARY:

An aliquot of the sample undergoes high temperature oxidation in a combustion tube maintained at 1050°C. Oxidation of the sample converts the chemically-bound nitrogen to nitric oxide (NO) and the sulphur to sulphur dioxide (SO_2).

In the nitrogen detector, ozone reacts with the nitric oxide to form excited nitrogen dioxide (NO_2). As the NO_2 reverts to its ground state, chemiluminescence occurs and this light emission is monitored by a photomultiplier tube. The light emitted is proportional to the amount of nitrogen in the sample.

In the sulphur detector, the sulphur dioxide is exposed to ultraviolet radiation and produces a fluorescent emission. This light emission is proportional to the amount of sulphur, and is also measured by a photomultiplier tube.

Quantitation is determined by a comparison to the responses given by standards containing carbazole and dimethyl sulfoxide in xylene.

SAFETY CONSIDERATIONS:

1. Compressed gases should be handled with care.
2. Dimethyl sulphoxide: irritant, flash point 95°C. Harmful if absorbed through the skin. May cause allergic skin irritation. Avoid contact with skin and eyes.
3. Ozone: highly toxic by inhalation. Strongly irritating to the eyes and upper respiratory tract.
4. Xylene: flammable, flash point 25°C. Harmful if inhaled. Irritating to the skin and eyes.

WASTE DISPOSAL:

Dispose of all sample material and xylene in a suitable hydrocarbon storage tank.

APPARATUS, REAGENTS, AND MATERIALS:

1. Antek 701C Fluorescent Sulphur System and 703C Chemiluminescent Nitrogen System consisting of:
   - Model 720C Chemiluminescent Nitrogen Detector
   - Model 714C Fluorescence Sulphur Detector
   - Model 771C Pyroreactor
   - Model 735 Syringe Drive
   - Model 736 Autosampler
   - Trivector Data System
2. Analytical balance.
3. Volumetric flasks: 10, 25, 50 and 100 mL, Class A.
4. Autosampler vials: 2 mL capacity with teflon-lined seals.

REAGENTS:

1. Activated Charcoal
2. Carbazole, m.p. 244–246°C
3. Dimethyl Sulphoxide, m.p. 18.6°C
4. Drierite
5. Argon, 99.995%, Matheson
6. Oxygen, 99.995%, Matheson
7. Xylene, Certified ACS

SAMPLE CONSIDERATIONS:

Amount required:	10 mL
Destructive:	Yes
Properties:	Solid or liquid soluble in xylene

INSTRUMENT PARAMETERS:

1.	Pyrolysis temperature:	1050°C	
2.	Inlet temperature:	1050°C	
		Flow rate	Rotor meter
3.	Inlet argon	114 mL/min	3.5
4.	Inlet oxygen	10 mL/min	0.3
5.	Pyro oxygen	545 mL/min	3.0
6.	Ozone	30 mL/min	1.5
7.	System type	simultaneous or single channel	
8.	Sample type	liquid	
9.	Concentration units	PPT (channel A, sulphur)	
		PPM (channel B, nitrogen)	
10.	Weight units	mg	
11.	Send results to host port	yes	

INTEGRATION PARAMETERS:

1.	Run time	360 s
2.	Sample rate	1 s
3.	Input voltage	10,000 mV
4.	Start time	0 s
5.	End time	360 s
6.	Maximum variance	5%
7.	Autosampler	yes (manual mode: NO)
8.	Flush time	0.25 min (manual mode: 0.00)
9.	Injection dwell	10 s
10.	Syringe drive	yes
11.	X-axis scaling factor	1

CALIBRATION PARAMETERS:

1.	Calibration curve order	1
2.	Injections per level	3
3.	Calibration curve x-axis	area
4.	Calibration curve y-axis	concentration

PROCEDURES:

A. Preparation of Standards:

1. Prepare sulphur/nitrogen standards to cover the expected concentration range of the samples. Typically the calibration curve will range from 0.01% to 0.250% sulphur, and 10 ppm to 250 ppm nitrogen.
2. Weigh 0.30 g of carbazole into a 100 mL volumetric flask. Record the weight to 0.0001 g. This will give a solution containing approximately 250 ppm nitrogen.
3. Weigh 0.60 g of dimethyl sulphoxide (DSMO) into the same 100 mL volumetric flask. Record the weight to 0.001 g. This will give a solution containing approximately 0.25% sulphur.
4. Dilute to volume with xylene.
5. Calculate the exact concentration of the standard solution.

$$\%\,S = wt\ DSMO\ (g) \times \frac{32.066}{78.13}$$

$$ppm\ N = \left[wt\ carb\ (g) \times \frac{14.007}{167.21} \right] \times 10{,}000$$

5. Calculate the exact concentration of the standard solution.
6. Perform serial dilutions to prepare the remaining standard solutions.

   2 mL to 50 mL = 0.01% S, 10 ppm N

   10 mL to 50 mL = 0.05% S, 50 ppm N

   20 mL to 50 mL = 0.10% S, 100 ppm N
7. Calculate the exact concentration of the standard solutions. These values are entered into the calibration data table, sulphur onto channel A and nitrogen onto channel B.
8. Subsample the standard solutions into the autosampler vials.
9. Standards may be stored in the air-tight autosampler vials for up to three weeks.

B. Preparation of Samples:

1. A weight of sample is diluted to volume with xylene such that the expected concentration falls within the range of the calibration curve.
2. Record the sample weight to 0.0001 g.
3. Record the dilution volume.
4. Calculate the special units factor for each sample. This value is to be entered into the sample table on each channel.

$$special\ units\ factor = \frac{dilution\ volume\ (ml)}{sample\ weight\ (g)}$$

for undiluted samples:

$$special\ units\ factor = \frac{1}{density}$$

5. Subsample the sample solutions into the autosampler vials.

C. Start-Up Procedure:

1. Should the power be lost to the integrator, reload the software as per the instructions in Appendix A.
2. Update the time and date as necessary.
3. Replace the injection port septum and the diverter valve septa. This is required after approximately 100 injections.
4. Ensure that the furnace temperatures are correct (~1050°C).
5. Ensure that the gas flows are correct, as listed above, and that there is enough for the day's operation.
6. Turn on the ozonator and the UV source using the toggle switches located on the rear panel of the detectors. Allow at least 30 minutes warm up time.
7. Do a manual zero check:
   - Place manual/automatic push button to manual.
   - Set attenuation to 1.
   - With the zero adjust, bring microamp null meter to zero.
   - Place manual/automatic to AUTO.
   - Select the proper attenuation, typically the sulphur detector is set to 20 and the nitrogen detector is set to 5.
   - Depress the reset to zero the microamp null meter.
8. Select the system to be run as single channel or simultaneous.

D. Analysis of Standards:

1. Enter the calibration standards and their respective concentrations into the calibration sequence table; if running the system as simultaneous, enter the data into both channel A and B.
   - From main screen, enter calibration set-up menu (F2).
   - Enter the calibration sequence table (F1).
   - Enter the standard name and concentration.
   - Sulphur standards are entered into channel A, nitrogen standards into channel B.
   - To return to the main menu, depress ESCAPE.
2. Load the standards in the autosampler tray in the same order as they appear in the calibration sequence table and position the tray to inject the first standard.
3. Ensure that there is to be a printed copy of the standard analysis, indicated by a HARD COPY YES in the method edit menu.
4. Start the analysis by selecting RUN CALIBRATION STANDARDS (F5).
5. When the calibration run has been completed, obtain a printed copy of the calibration curves (F2 on the calibration set-up menu) to ensure that the calibration is correct.

E. Analysis of Samples:

1. Enter the sample tag number and the special units factor for each sample into the sample table, channel A for sulphur analysis and the channel B for nitrogen analysis. Enter data into both tables when

running the system simultaneously.

- From main screen, select sample table edit (F7).
- Enter data for each sample.
- To return to main screen, depress ESCAPE.
- To change to other channel select change channel (F10).
- Re-enter all data on the second channel.

2. Note: One sample is run as a duplicate to ensure that there was no baseline drift during the analyses time.
3. Load the autosampler with the samples in the same order as they appear in the sample table, and position the tray to inject the first sample.
4. Samples are typically run without a printed copy of each analysis. Enter the method edit menu (F3) and enter HARD COPY NO. Return to the main menu.
5. Start the analysis of the samples by depressing "RUN UNKNOWN" (F8).
6. At the completion of the analysis, obtain a report of the analysis by depressing "REPORT" (F6) for both the sulphur and the nitrogen channels.

INSTRUMENTATION SHUTDOWN:

1. Switch off the ozonator and the UV source using the toggle switches located at the rear of the detectors.
2. Oven temperatures remain at their normal settings.

APPENDIX A:

To start CRT after power has been interrupted, press DEL key (on keyboard) while turning on the power switch located on the back of the CRT unit until the system prompt is displayed. The unit can then be restarted using the function key (F11).

The start-up command is incorporated to function key (F11) as follows:

1. Press LOCAL key.
2. Press SET UP key.
3. Press (I) down arrow key twice. The cursor will be located at "Set-Up function keys."
4. Press RETURN key.
5. Press F11.
6. Type CHAIN "R: ANTEK (m*) " RETURN.
7. Press SET UP key twice.

ROUTINE MAINTENANCE:

Daily:

1. Change the injection port septum and the autosampler diverter valve septa. Septa require changing after approximately 100 injections.
2. Check the manual zero as explained in the start-up procedure.

Monthly:

1. Replace the air filters on the rear of the detectors and on the furnace.

2. Clean and re-grease the ball joint fitting on the pyrolysis tube.
3. Clean and re-grease the fittings on the syringe drive unit.

As Needed:

1. Empty and recharge the charcoal/drierite scrubber with fresh material when the drierite changes colour.
2. Clean and/or replace the pyrolysis tube.
3. Replace the teflon ferrules.

Yearly:

1. Perform electronic adjustments as per Section 8.3 of the Service Manual.
2. Clean the fluorescence chamber and the chemiluminescent reaction chamber as per Section B.4 of the Service Manual.

3

HYDROCARBON CHARACTERIZATION

Existent Dry Sludge by Hot Filtration Test

INTRODUCTION: Dry sludge is defined as the material separated from the bulk of an oil by filtration and which is insoluble in heptane (1). Existent dry sludge is the dry sludge in the original sample as received and is distinguished from the accelerated dry sludge obtained after aging the sample by chemical addition or heat. The test is used as an indicator of hydrocracker operability and as a measure of potential downstream fouling (2).

SCOPE: This method describes the determination of existent dry sludge in hydrocracker feed and bottoms by the hot filtration method. The filtration is described as occurring at 150°C, but the filtration temperature may be selected in the 100 to 200°C range and reported with the results.

SUMMARY: The homogeneous and undiluted sample is passed through a pair of Whatman GF/A filters at 150°C. The residual material on the filters is washed with warm heptane (65°C) and the filters are dried for one hour at 110°C. The incremental weight of the bottom filter as a result of the filtration and solvent wash is taken as an oil adsorption correction and is subtracted from the incremental weight of the top filter. The existent dry sludge is calculated as the non-filterable material corrected for oil adsorption and expressed as a percentage of the original sample weight. The average of duplicate determinations is reported.

BACKGROUND: Existent dry sludge is operationally defined as the material separated from the bulk of an oil by filtration and which is insoluble in heptane. It was originally developed in the early 1950's to measure the cleanliness of residual fuel oils (3). The application to hydrocracking involves the measurement of the insoluble components in the sample. The key to the filtration is a pair of glass fibre filters of 1.6 μm porosity clamped between a filtration vessel and a filtration funnel (Figure 1). A Resistance Temperature Dependent (RTD) sensor is mounted in the filtration vessel in close proximity to the filters. A controller compares the measured temperature with the desired filtration temperature to determine the power to be supplied to a heating unit (Figure 2) that slides over the filtration vessel. The heating unit achieves the desired temperature by balancing the heat generated by cartridge heaters and the cooling of an air purge. The sample and filtration vessel are pre-heated to the desired temperature, and the sample is transferred to the filtration vessel. When the filtration is complete, the filters are washed with warm heptane, dried, and weighed. The weight increase of the bottom filter is used as an adsorbed oil correction for the top filter. The existent dry sludge is the weight increase of the top filter corrected for oil adsorption expressed as a percentage of the sample.

Increasing temperature reduces viscosity and improves filterability. The filtration temperature, however, should not produce any visible degradation of the sample. The apparatus may also be configured to allow for optional purging of the hot sample with nitrogen. Designing variable temperature capability into equipment speeds up the analysis time and expands the range of samples amenable to the method. Since the test is operationally defined, it can be applied to any sample. Normally the test is applied to hydrocracking bottoms. Heavy samples such as bitumen, may give poor precision or report as "WNF" (would not filter).

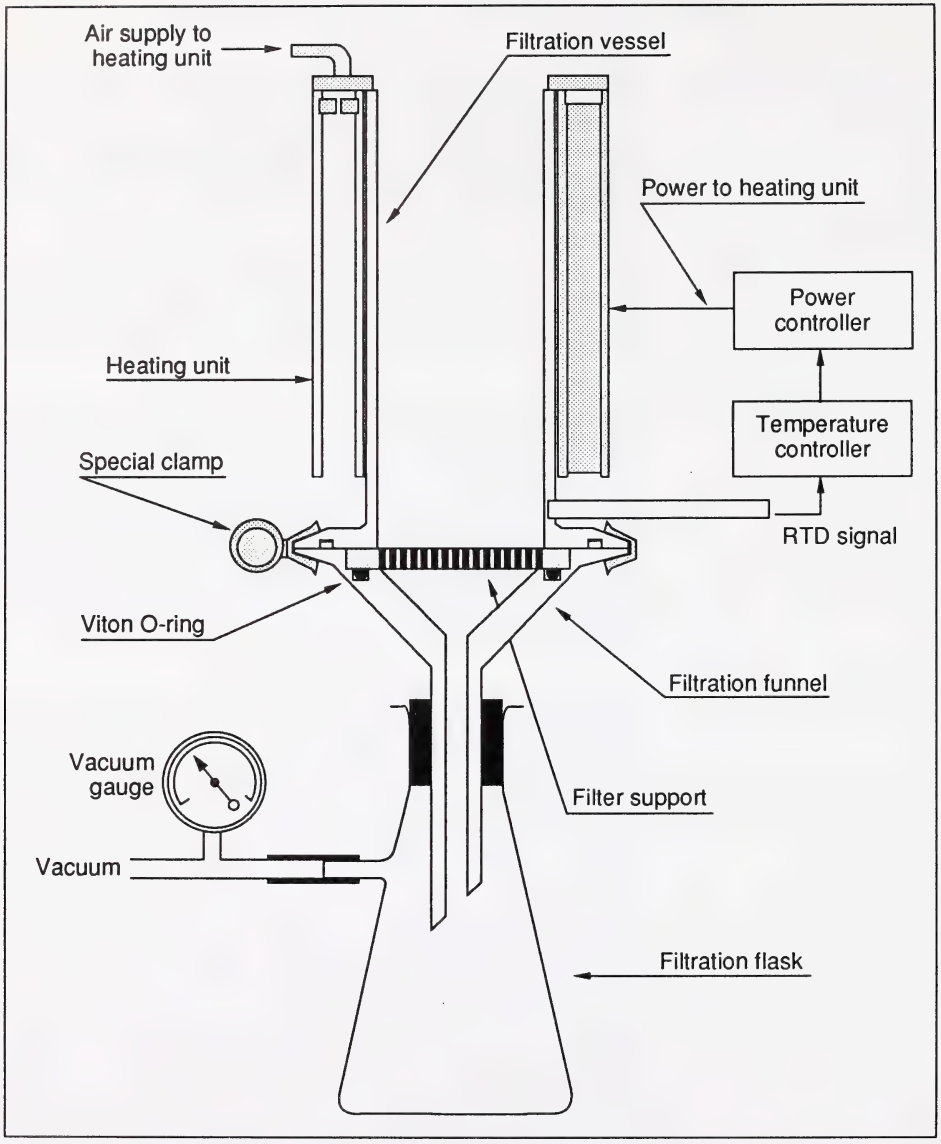

Figure 1. Schematic of the hot filtration apparatus.

Another feature of streams arising from oil sand processing and subsequent upgrading is the presence of extraneous material; e.g., clay, sand, rust, coke, catalyst fines. This material is included in the existent dry sludge and can contribute to loading problems with the filter. The filtration uses the large 55 mm diameter glass fibre filters to improve filterability. By dissolving a separate aliquot in toluene and using the same filtration apparatus the extraneous material can be independently determined and used to assist in the interpretation of the existent dry sludge.

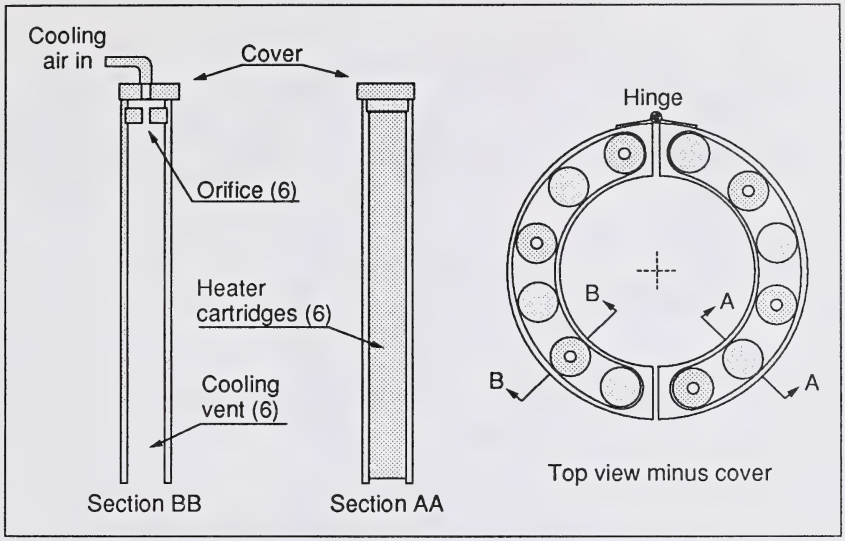

Figure 2. Heater enclosure assembly.

SAFETY CONSIDERATIONS:

1. Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis.
2. Heptane: highly flammable.
3. Hot surfaces (e.g., 150°C) may cause severe burns and provide a source of ignition for flammable materials.

APPARATUS, REAGENTS, AND MATERIALS:

1. Filtration apparatus, as illustrated in Figure 1. Fabrication of the equipment is illustrated in principle in Reference 3. Our implementation:
   a. Uses the heater enclosure shown in Figure 2 to slide over a filtration vessel. Heater cartridges are used in alternate slots of the heater enclosure.
   b. Tapers the circumference of filtration vessel and filtration funnel to permit use of the clamp shown in Figure 3. This clamp provides uniform pressure on the filter and permits easy assembly/disassembly.
   c. Employs a filter support containing a large number of randomly placed 1 mm holes.

   An example list of equipment for the temperature control is given in Table 1. This equipment is supplemented with a three-piece insulating jacket fabricated to fit the completed assembly.
2. Filter discs: glass fibre, Whatman GF/A, 55 mm diameter.
3. Oven: temperature 110°C.
4. Test jars: pour point test jars as described in ASTM D 97.
5. Thermometer with detachable probe: Technoterm Model 7200.
6. Vacuum: capable of maintaining a 700 mm Hg vacuum.

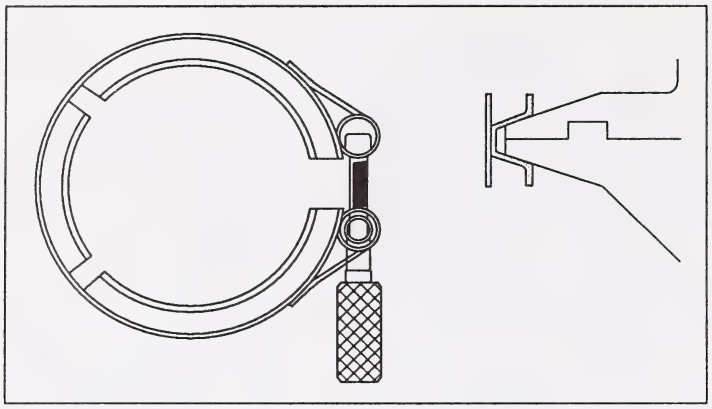

Figure 3. Special clamp.

7. Watch glasses.
8. Sand bath: Tecam Model SBL-1, temperature control to 260°C, equipped with cover to accept test jars and prevent loss of sand from the bath.
9. Rotameter: Brooks tube size R-6-15-B with steel float.
10. Hot plate: explosion proof, 260°C maximum.
11. Heptane: reagent grade.
12. Toluene: reagent grade.
13. Analytical balance: readable to 0.1 mg.

SAMPLE CONSIDERATIONS:

Amount Required: 25 g
Destructive: Yes

PROCEDURES:

1. Heat the sample in an oven at 60°C for one hour before shaking to uniformly disperse any sludge in the oil. Place subsamples of appropriate size for the hot filtration test, e.g., 10 g for bottoms and 5 g for feed, in the pour point test jars. Two subsamples are selected in order to perform duplicate determinations for each sample. Place a temperature probe in each pour point jar and determine the weight of sample, jar, and temperature probe to the nearest 0.01 g.

Table 1. Example hardware for temperature control of hot filtration test

- Heater Cartridges: 57 V, 300W Varian P.N. 22-000049-00
- Process Controller: Analogic Corp. AN25C06-2-3-X-l-P-X-X-10-C-X
- Power Controllers: Eurotherm Corp. Amstack Solid State Contactor Model ASl 4-20 ma input, 10 amp output
- RTD: 100 ohm, Platinum Pt100 per DIN 433760 Alpha = 0.00385
- RTD Connectors: Male and Female 1034-CU
- Size D Silverflex Sleeving
- Terminal Strip
- Phoenix Contact: Min-pack U.K. 2.5
- Hammond Cabinet: 1414PH010 Panel Box
- Amphenol Military Spec: 8 pin connector, 97-18-8S insert, 97-3101A-18 cable receptacle, 97-3106B-18 split shell, 97-18-8P insert, 97-3057-1010 cable clamp, 9779-513-10 bushing

2. For each test, dry two GF/A filters for 20 minutes in an oven at 110°C. Remove the filters from the oven and store in a desiccator to cool and keep dry until required. Weigh the two filters required for the test, separately, to the nearest 0.1 mg. Handle the filters with tweezers. For identification place the filters on clean, labelled watch-glasses.
3. Attach a filter flask to the funnel of the filter assembly with a rubber stopper. Using vacuum tubing, connect the filter flask to the vacuum gauge and pump.
4. Ensure the inside of the filtration vessel is clean. If required the funnel, sample chamber of the filtration vessel, and filter support may be cleaned by wiping with a Kimwipe moistened with toluene. Place the filter support in the funnel and stack the two previously dried and weighed filters on top of the support. Ensure that the filters are positioned at the centre of the support. Place the filtration vessel in position on top of the filters. Clamp the filtration vessel to the funnel so that uniform pressure is applied to the filters and an effective seal is obtained. Place the heating jacket over the filtration vessel and ensure that it is plugged into the power controller. Also connect the RTD to the temperature controller and turn on the controller. Set the temperature controller to 150°C. Fasten the three-piece insulating jacket around the hot filtration unit. Turn on the cooling air flow for the heating unit and adjust to 0.1 L/s.
5. Turn on the air flow to the sand bath to provide gentle circulation of the sand, and ensure the sand bath temperature controller is set to 150°C. After the sand bath and filtration vessel have equilibrated for at least 900 s at 150°C, place the pre-weighed pour point test jar with sample and temperature probe in the opening of the sand bath cover. Attach a clamp to the test jar to hold it in position in the sand bath and stir the sample with the temperature probe during heating. When the contents of the jar reach 150 ± 2°C, pour the contents onto the centre of the filter. Ensure no sample is poured along the inside wall of the sample chamber. After the sample jar cools, weigh the jar, temperature probe, and residual sample.
6. Turn on the vacuum. Filter the sample until the surface of the upper filter is dry. If the filtration time exceeds 60 minutes, repeat the analysis with a smaller sample (minimum sample 4 to 5 g). If the filtration time with the smallest sample exceeds 60 minutes, terminate the analysis and report the result as WNF (Would Not Filter).
7. Change the temperature set point of the controller to 65°C and remove the insulating jacket from around the heating unit. Warm three 50-mL portions of heptane on a hot plate to 65°C. When the filtration apparatus and heptane aliquots have reached 65°C, rinse the filter with three separate aliquots of the warm heptane. Pour each aliquot as a whole onto the filter to ensure total wetting and washing. Do not remove or transfer any bituminous deposit from the wall of the filtration vessel to the filter.
8. Turn off the temperature controller, remove the heating unit and then the filtration vessel. If the outer edge of the filter is darkened, oil leakage is indicated and the procedure needs to be repeated. If the filter edge is not darkened, remove the filters and place in marked weighing dishes. Dry the filters at 110°C for 60 minutes. Cool the filters in a desiccator for 30 minutes and weigh each of the filters.
9. Clean the apparatus with toluene.

CALCULATIONS:

1. Calculate the existent dry sludge content of each subsample as:

$$\text{Existent dry sludge, \% (m/m)} = \frac{(m_2 - m_1) - (m_4 - m_3)}{m_s} \times 100$$

where m_s = mass of sample, g
m_1 = mass of upper filter before filtration, g
m_2 = mass of upper filter after filtration, g
m_3 = mass of lower filter before filtration, g
m_4 = mass of lower filter after filtration, g

2. Calculate the existent dry sludge content of the sample as the average of the existent dry sludge contents of the two subsamples. Ensure the duplicate determinations are consistent with the precision for the sample type being analyzed.

REPORT FORMAT:

Report the existent dry sludge content of the sample to the nearest 0.01% (m/m). Also report the sample size as: "on a 10 g sample portion," or "on a 5 g sample portion." Report the temperature at which the filtration was performed, e.g., 150°C. If the filtering time exceeds 60 minutes for a 5 g sample portion report as WNF (Would Not Filter).

PRECISION:

For LC-Finer bottoms, relative standard deviations of 1.02% and 1.07% were obtained on five determinations of the existent dry sludge by two different operators. For a bitumen feed, a relative standard deviation of 9.9% on the existent dry sludge has been determined.

TIME CONSIDERATIONS:

Time Per Analysis:	5 h
Technologist Contact Time:	1.25 h
Samples Per Time Period:	4–6/8 h
Calibration Time:	None

REFERENCES:

1. Shell Method Series, "Existent and Dry Sludge Contents of Residual Fuel Oils — Modified Hot Filtration Test," SMS 2696-83, Shell International Research Maatschappij B.V.
2. Van Driesen, R.P. and Strangio, Rhoe A., "The High Conversion LC-Fining Process," AIChE 1986 Spring National Meeting, New Orleans, Louisiana, April 6–10, 1986.
3. Lewis, C.P.G., Quillet, R., and Schreuder, T., "Resid Fuel-Oil Stability, Cleanliness Test Improved," Oil and Gas Journal, April 1985, p. 73.

Extraneous Material by Filtration

INTRODUCTION: Extraneous material is defined as the toluene-insoluble component of bituminous samples. The extraneous material may contain clay, sand, rust, coke, or catalyst fines. The test is used to complement the hot filtration test by providing a measure of the extraneous component in the existent dry sludge.

SCOPE: This method describes the determination of extraneous material in bituminous samples by the filtration method.

SUMMARY: The sample is dispersed in toluene and filtered at room temperature through dried and pre-weighed Whatman GF/A filters. After drying the filters the extraneous material is calculated as the percentage of the original material remaining on the filters. The average of duplicate measurements is reported.

BACKGROUND: Extraneous material is determined as the percentage of toluene-insoluble material in the sample. The method described here arises from use of the results to complement interpretation of the hot filtration test. Consequently the apparatus and filters employed are those described in the hot filtration test. However, the analyst may choose to substitute a less expensive or more convenient alternative.

The extraneous material is operationally-defined and its application can be extended to diverse samples. If filter loading gives filterability problems for a particular sample type, the method may be modified to first filter through a more porous filter and then through a second filter. Alternatively, some manufacturers provide glass fibre filters of variable porosity through the filter.

The apparatus described here is designed for 55 mm diameter filters. Some filter types are not readily available with a 55 mm diameter. In this case, an alternate filter support may be fabricated, e.g., consisting of two pieces with the same combined external dimensions as the single support used in the hot filtration test. The top piece provides a taper to allow filters of smaller diameter, and the bottom piece provides support for the filters.

SAFETY CONSIDERATIONS AND MATERIALS: Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis.

APPARATUS, REAGENTS,

1. Filtration apparatus, as illustrated in Figure 1. Fabrication of the equipment is described in the "Existent Dry Sludge by Hot Filtration Test" method (Section 3.1).
2. Filter discs, glass fibre, Whatman GF/A, 55 mm diameter.
3. Oven, temperature 110°C.
4. Test jars, pour point test jars as described in ASTM D 97.
5. Vacuum, capable of maintaining a 700 mm Hg vacuum.
6. Watch glasses.
7. Toluene, reagent grade.
8. Analytical balance readable to 0.1 mg.

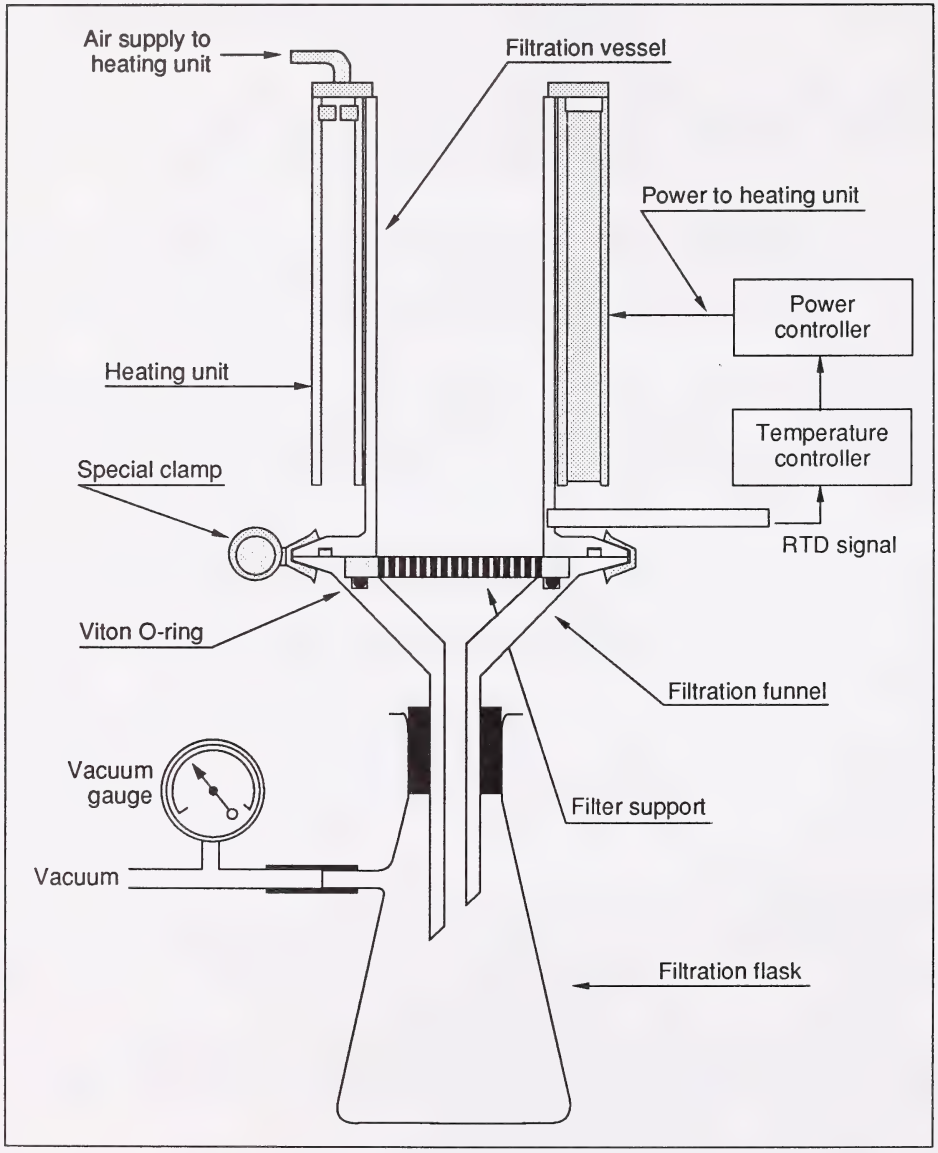

Figure 1. Schematic of the hot filtration apparatus.

SAMPLE CONSIDERATIONS:

Amount Required: 25 g
Destructive: Yes

PROCEDURES:

1. Heat the sample in an oven at 60°C for 60 minutes before shaking to uniformly disperse insoluble material. Place subsamples of appropriate size for the extraneous material determination, e.g., 10 g for bottoms and 5 g for feed, in the pour point test jars. Two subsamples are selected in order to perform duplicate determinations for each sample. Determine the weight of each sample and jar to the nearest 0.01 g. Completely disperse each sample in 50 mL of toluene.
2. For each test, dry two GF/A filters for 20 minutes in an oven at 110°C. Remove the filters from the oven and store in a desiccator to cool and keep dry until required. Weigh the two filters required for the test separately, to the nearest 0.1 mg. Handle the filters with tweezers during manipulations. For identification purposes place the filters on clean numbered watch-glasses.
3. Attach a filter flask to the funnel of the filter assembly with a rubber stopper. Using vacuum tubing connect the filter flask to a vacuum gauge and pump.
4. Ensure the inside of the filtration vessel is clean. If required the funnel, sample chamber of the filtration vessel, and filter support may be cleaned by wiping with a Kimwipe moistened with toluene. Place the filter support in the funnel and stack the two previously dried and weighed filters on top of the support. Ensure that the filters are positioned at the center of the support. Place the filtration vessel in position on top of the filters. Clamp the filtration funnel to the funnel so that uniform pressure is applied to the filters and an effective seal is obtained.
5. Transfer the dispersed sample completely into the filtration vessel. When filtration is completed, rinse the filter with toluene until the passing toluene is clear. Remove the clamp and filtration vessel. Ensure the outer edge of the filter is white. If the edge is darkened a leakage is indicated and the procedure needs to be repeated. Remove the filters and place on a watch glass labelled for identification. Dry the filters at 110°C for 60 minutes. Cool the filters in a desiccator before reweighing them.
6. Clean the apparatus with toluene.

CALCULATIONS:

1. Calculate the extraneous matter in the subsample as:

$$\textit{Extraneous matter, \% (m/m)} = \frac{m_2 - m_1}{m_s} \times 100$$

where: m_s = mass of sample, g
m_1 = mass of GF/A two filters before filtration, g
m_2 = mass of GF/A two filters after toluene wash, g

2. Calculate the extraneous matter for the sample as the average of the extraneous matter for the two subsamples. Ensure the duplicate determinations are consistent with the precision for the sample type being analyzed.

REPORT FORMAT: Report the extraneous material in the sample to the nearest 0.01% (m/m).

PRECISION: The measurement of extraneous material for LC-Finer bottoms has displayed a relative standard deviation of 1.3% on five determinations.

TIME CONSIDERATIONS:

Time Per Analysis:	2.5 h
Technologist Contact Time:	1.0 h
Samples Per Time Period:	6–8/8 h
Calibration Time:	none

Determination of Specific Gravity and Density of Bituminous Materials by Pycnometer

INTRODUCTION:

This method is routinely used to measure the density of samples being charged to a distillation flask, where volume charge is needed, but the volume is not conveniently measured. The volume may be found by weighing the sample, and determining the sample density. It is also used in routine measurements of material properties.

Note that even a small amount of solids in the sample will influence its measured density. One percent solids was shown to raise the density by 0.007 g/cm^3.

SCOPE:

1. This method covers the determination of the specific gravity and the density of bituminous samples at 25°C with the use of a pycnometer. This method is based on ASTM D70 (1).
2. Only high viscosity samples, with density equal to or greater than water, are measured. Other samples are measured using the Digital Densimeter.

SUMMARY:

1. The specific gravity of the sample is determined from the ratio of the weight of a given volume of the sample at 25°C to an equal volume of water at the same temperature.
2. The density is calculated by multiplying the specific gravity by the density of water at 25°C.

SAFETY CONSIDERATIONS:

No unusual safety considerations.

WASTE DISPOSAL:

Dispose of sample materials in a manner appropriate to the nature of the sample, keeping in mind that some reactor product streams may contain carcinogenic materials.

APPARATUS, REAGENTS, AND MATERIALS:

1. Glass pycnometer, Hubbard or Hubbard-Carmick design, conforming to ASTM D70 specifications.
2. 600-mL glass beakers.
3. Constant temperature water bath, Haake Model D8-13 or equivalent (control to ± 0.05°C).
4. Thermometer, conforming to ASTM specification E1.

SAMPLE CONSIDERATIONS:

Amount Required:	25 mL of sample
Properties:	Liquid samples must be more dense than water at the measurement temperature.
Interferences:	Gas bubbles entrapped in the liquid sample will lead to erroneously low results.
Destructive:	No

PROCEDURES:

Preparation of Equipment:

1. Fill a 600-mL beaker with freshly distilled or de-ionized water and place in a constant temperature water bath.

2. Maintain the temperature of the water bath at 25°C.

Calibration of Pycnometer:

1. Clean, dry, and weigh the pycnometer to the nearest 0.1 mg. Designate this weight as "A."
2. Fill the pycnometer with freshly boiled distilled or de-ionized water, insert the stopper taking care to avoid the formation of air bubbles, and immerse the pycnometer into the beaker containing distilled water. Allow the pycnometer to equilibrate for at least 30 minutes.
3. Remove the pycnometer and immediately dry the top of the stopper with one stroke, dry the remaining outside area of the pycnometer and weigh to the nearest 0.1 mg. Designate this weight as "B."

Determination of Specific Gravity:

1. Heat the sample (50°C oven for one hour) to a fluid condition and transfer into the clean, dry pycnometer, fill to approximately 3/4 capacity taking care to keep the material from touching the sides of the pycnometer above the final volume and to avoid the inclusion of air bubbles.
2. Insert the stopper and intermittently apply a gentle vacuum to the opening in the stopper. This helps to remove included air bubbles.
3. Allow the pycnometer and contents to cool to ~25°C on the laboratory bench for 90 minutes.
4. Weigh the pycnometer and contents to the nearest 0.1 mg. Designate this weight as "C."
5. Fill the remaining volume of the pycnometer with distilled or de-ionized water, insert the stopper taking care to avoid the formation of air bubbles, and immerse the pycnometer into the beaker containing distilled water. Allow the pycnometer and contents to equilibrate for not less than 60 minutes.
6. Remove and weigh the pycnometer using the same technique as in the calibration procedure. Designate this weight as "D."
7. Each sample is assayed in duplicate.

CALCULATIONS:

1. $$\text{Specific gravity} = \frac{(C - A)}{(B - A) - (D - C)}$$

   where: A = weight of pycnometer
   B = weight of pycnometer plus water (filled)
   C = weight of pycnometer plus bitumen
   D = weight of pycnometer plus bitumen plus water (filled)

2. Density = specific gravity x W(t)
   where W(t) = density of water at the test temperature*
3. The density obtained at 25°C may be converted to density at other temperatures using Table 53 of the ASTM-IP Petroleum Measurement Tables.

* From the Handbook of Chemistry and Physics the density of water at 25°C is equal to 0.9971 g/cm^3.

REPORT FORMAT: Report the density obtained to the nearest 0.0001 g/cm^3.

PRECISION: The precision of the method was evaluated by assaying three different samples on each of three different days. The means and standard deviation(s) are given below:

- 1983 bitumen 1.0157 ± 0.0003 g/cm^3
- 1985 bitumen 1.0170 ± 0.0007 g/cm^3
- 1986 bitumen 1.0202 ± 0.0017 g/cm^3

TIME CONSIDERATIONS:

Time Per Analysis:	6 h
Technologist Contact Time:	30 min
Samples Per Time Period:	6/d

REFERENCES: ASTM Method D70, "Specific Gravity and Density of Semi-Solid Bituminous Materials."

Determination of Hydrocarbon Density Using an Anton Parr Densimeter

INTRODUCTION: Density is a fundamental physical property which, in conjunction with other physical properties, can be used to characterize bituminous samples.

SCOPE: This method determines the density of a homogeneous hydrocarbon material which can be handled by a syringe or an automatic sampling device.

SUMMARY: This method uses an instrument that measures the total mass of a tube by determining its natural frequency of vibration. This frequency is a function of the dimensions and the elastic properties of the tube, and the weight of the tube and contents. Calibration with water and air provides data for the determination of the instrument constraints which allow conversion of the natural frequency of vibration to sample density.

SAFETY CONSIDERATIONS: Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes. May cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through the skin and may cause dermatitis.

APPARATUS, REAGENTS, AND MATERIALS:

1. DMA 48 Digital Densimeter. Anton-Parr K.G., A-8054 Graz, Postfach 17 Kamtner Strasse, Austria. This instrument is equipped with a sample pump which automatically draws the liquid from the sample bottle and also has an adaptor for filling with a Leur syringe.
2. Syringe: 2 mL.
3. Toluene: A.C.S. Reagent Grade.

SAMPLE CONSIDERATIONS:

Amount Required:	10 mL
Destructive:	No
Properties:	Liquid, particulate- and water-free hydrocarbon phase.

PROCEDURES:

Calibration of Instrument:

1. Two standards are required for calibration. Their density values must differ by more than 0.01 g/cm^3 and must cover the total density range required.
2. The standards used, in this case, are air and water, but can be any two liquids of known densities.
3. Set the temperature (e.g., 20°C, 50°C, etc.).
4. Enter F100 (for air, see instrument manual). Display will show the calculated density of air at 20°C. Enter this value: display will show period for air at 20°C.
5. Read pressure from barometer and convert, from table in manual, to 20°C and enter this value.
6. Wait for air density to appear on display, e.g., 0.0011/20°C.
7. Switch on illumination.
8. Fill the tube with distilled water.

9. Enter F101 (calibration for water, see manual).
10. Press "ENTER" and wait. Display will show density of water at 20°C.
11. Calibration is complete.

Sample Measurement:

Using the FRS (filling and rinsing system) mode.

1. Enter the parameters as given in the manual.
2. Put the tube in the sample.
3. Press the "ACTIVATE" key and then read the density when the display starts flashing.
4. The instrument will then automatically clean and dry the tube ready for the next sample.

Manual Method:

1. Switch on the illuminator of the oscillator cell.
2. Fill the syringe with the sample and then fill the oscillator tube ensuring that there are no gas bubbles in the tube.
3. Switch off the light.
4. Read the density when the display stops flashing.
5. Clean the oscillator tube with toluene and dry thoroughly.

CALCULATIONS: Not applicable.

REPORT FORMAT: The density is reported to the nearest 0.0001 kg/L.

PRECISION AND ACCURACY: For pure compounds, repeat measurements by the same operator typically agree within ±0.0001 kg/L. The variability observed among nine operators, measuring the same pure compounds, is shown below.

Compound	Mean kg/L	S.D. kg/L	% RSD
Toluene	0.8670	± 0.0004	0.04
Isopropyl alcohol	0.7859	± 0.0002	0 02
n-Heptane	0.6834	± 0.0003	0.05

TIME CONSIDERATIONS:

Time Per Analysis:	5 min
Technologist Contact Time:	5 min
Samples Time Period:	60 d
Calibration Time:	15 min

Determination of Refractive Index of Hydrocarbon Liquids

INTRODUCTION:

In a critical angle refractometer, light is directed at the interface between a prism and the sample at a range of angles. At the critical angle the light changes from penetrating the sample to being totally reflected back into the prism from the interface. Knowing the angle at which this happens, and the properties of the prism, the refractive index (R.I.) may be found. The specified unit measures this angle, applies appropriate corrections if required, and displays the refractive index directly on a digital display. The temperature of the prism may also be displayed. The advantage of the critical angle unit is that the light is not passed through the sample, as in the Abbe refractometer. This makes the critical angle unit suitable for highly-coloured liquids as well as clear liquids, in contrast to the Abbe which cannot measure dark liquids.

A critical angle refractometer measures the very thin layer of liquid which contacts the prism, typically the continuous phase of the sample. It will frequently not be influenced by suspended or dispersed material in the sample. Emulsions and very fine dispersions may influence the unit. A particulates-free, single phase sample is far better, but one containing these inclusions is not automatically excluded.

The performance of the specified unit has generally been excellent. Anacon Instruments also makes a critical angle laboratory unit, but the Anacon instrument cannot determine as high an R.I. as the RIC-1 unit, and is incapable (at last report) of measuring bitumen (R.I. = 1.57) directly. The primary disadvantages of the RIC-1 unit are its cost, and the lack of local maintenance expertise.

This measurement is routinely performed on a wide variety of upgrading samples. It is used, along with other parameters, as an indicator of the degree of upgrading obtained.

SCOPE:

This method covers the measurement of the refractive index of liquid petroleum products in the range of 1.3300 to 1.6500. Typically the measurement is carried out at 20°C. The instrument is capable of operation from 5°C to 40°C.

SUMMARY:

1. A commercially-available critical angle automatic refractometer (Index Instruments, Model RIC-1) is used for the determination of refractive index.
2. Approximately 1 mL of sample is applied to the clean, dry prism surface. The sample must completely cover the prism surface, and contain no air bubbles, particulates, or dispersed phase which settle onto the prism surface. Particulates or dispersed phase falling onto the surface is typically shown by a steady drift of the readings, even after the temperature should be stable. The instrument is calibrated by measuring pure water, and checked against calibration standards.

SAFETY CONSIDERATIONS:

1. Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis.
2. Acetone: highly flammable, flashpoint –9°C. Moderately toxic by inhalation.

WASTE DISPOSAL:

1. Dispose of oily Kimwipes into a covered waste can, for disposal in a manner appropriate to the sample nature.
2. Discard excess sample in a manner appropriate to the nature of the sample.

APPARATUS, REAGENTS, AND MATERIALS:

1. Automatic Refractometer,
   Index Instruments,
   Model RIC-1
   North American Representative:
   Prism Instruments Inc.,
   P.O. Box 13308,
   New Orleans, Louisiana, USA
   Sold in Canada through:
   Terochem Laboratories,
   P.O. Box 8188, Stn. "F",
   Edmonton, Alberta
   T6H 4P1
2. Pasteur pipettes.
3. Toluene.
4. Acetone.
5. Refractive Index standards (1.4600 – 1.6400 ± 0.0002), R.P. Cargille Laboratories Inc., Cedar Grove, New Jersey, USA 07009.

SAMPLE CONSIDERATIONS:

Amount Required:	10 mL
Destructive:	Yes
Properties:	Liquid, preferably particulates-free and single phase (see Introduction), with a refractive index within the instrument range.

PROCEDURES:

Calibration:

Preparation of standards:

The standards are used as purchased from the manufacturer. De-ionized water serves as the water sample.

Implementation of Standards:

1. Ensure the instrument has reached operating conditions in terms of temperature regulation and electronics stabilization.
2. Clean the prism surface with toluene and acetone using Kimwipes. Avoid scratching the surface. Allow the surface to air-dry.
3. Apply to the prism surface approximately 1 mL of de-ionized water using a Pasteur pipette. Ensure the surface is completely covered and that there are no entrapped air bubbles.
4. Replace the cover.
5. Wait until the temperature has reached 20°C and the refractive index value no longer drifts.

6. Record the value. The refractive index of water should be 1.3330 at 20°C.
7. Press the ZERO button to calibrate the instrument with water as a zero reference. Check the reading again for water. Note: The refractometer will automatically calculate and set the refractive index for water at any temperature up to 40°C.
8. Clean the water from the instrument surface.
9. Check/repeat this calibration at least once every 12 samples and at the start of a new set of samples.
10. Choose a standard in the estimated range of the samples to be run. Determine and record the refractive index of the standard and the measurement temperature.
11. If the reading obtained does not match that of the certified reference standard, re-zero, and check the instrument operation. If the value obtained still does not match, try another reference standard. Do not run the samples until a match with a certified standard is obtained.
12. Prepare the prism surface to run the samples. Clean with toluene and acetone.

SAMPLE ANALYSIS:

1. Ensure that the prism surface is clean using toluene and acetone. Air-dry the surface.
2. Apply to the surface approximately 1 mL of sample using a Pasteur pipette.
3. Ensure that the cell is evenly covered and that no air bubbles are present.
4. Replace the cell cover.
5. Check the operating temperature, frequently, to ensure the desired temperature has been achieved.
6. Check the refractive index until stable, then record the temperature and the refractive index.
7. Prepare the instrument for the next sample.
8. Run the selected standard and water reference at least once for every 12 samples or at least once in the total sample set if there are less than 12 samples.

CALCULATIONS:

None.

REPORT FORMAT:

The refractive index is reported to the nearest 0.0001 at the specified temperature.

PRECISION AND ACCURACY:

Precision:

Precision has been determined in our laboratory through the repeat analysis of a single sample by the same operator. Twelve measurements of this sample produced a mean of 1.5240 with a standard deviation of 0.0001. The measurement was performed at 20°C.

Accuracy:

Accuracy has been determined by comparison with a set of commercially-available liquid hydrocarbon reference standards (Table 1).

Table 1. Standards Measured at 25°C (03/02/86)

Standard value	Instrument result	Standard value	Instrument result
1.400	1.3993	1.520	1.5202
1.420	1.4188	1.540	1.5400
1.440	1.4395	1.548	1.5482
1.460	1.4602	1.552	1.5521
1.480	1.4799	1.556	1.5558
1.500	1.5001	1.560	1.5597
1.504	1.5038	1.580	1.5797
1.508	1.5078	1.600	1.5997
1.512	1.5118	1.620	1.6180
1.516	1.5160	1.640	1.6395
		1.660	1.6618

Standard values are quoted as "1.400 to 1.700, Adjustment ± 0.0002."

TIME CONSIDERATIONS:

Time Per Analysis:	10 min
Technologist Contact Time:	5 min
Samples Per Time Period:	6/h
Calibration Time:	15 min

Determination of Microcarbon Residue (MCR) of Bitumen, Heavy Gas Oils, and Light Gas Oils

INTRODUCTION:

The primary purpose of obtaining MCR data is to evaluate the amount of coke which would be formed from the material during coking operations. MCR is an indicator of the maximum capacity of the coking steps, which tend to be limited by total coke production rather than total feed rate. For this purpose MCR is applied to measure topped bitumen and residues from the hydroprocessing of bitumen, both of which are fed to the cokers.

MCR is also used to evaluate the reduction in coke-forming tendency produced by upgrading procedures. A wide variety of streams are measured for this purpose.

While MCR agrees well with Conradson Carbon Residue results, the degree of agreement is sample-related. In general the agreement between the methods has been within 0.6% MCR for samples we have studied, in the 10 to 16% MCR range.

SCOPE:

This method covers the determination of the amount of carbon residue left after evaporation and pyrolysis of petroleum products. This method is based on ASTM D4530-85.

SUMMARY:

A weighed quantity of sample is placed into a glass vial. This subsample is heated to 500°C under a nitrogen atmosphere for a specific time. The sample undergoes cracking and coking. Nitrogen is used to remove the volatile materials. The carbonaceous residue is reported as "% microcarbon residue" of the original sample.

BACKGROUND:

The Microcarbon Residue method is intended to provide a measure of the relative coke-forming properties of the sample under degradation conditions which simulate commercial coking operations. Ash-forming constituents and/or non-volatile constituents present in the sample will add to the residue value determined. The advantages of the current method over the SAM 4.020 and the Conradson Carbon Residue test (ASTM D189) methods used previously are:

- improved control of test conditions,
- smaller samples sizes,
- less operator attention,
- improved sample throughput.

SAFETY CONSIDERATIONS:

1. Compressed gases should be handled with care.
2. The condensate residue may have carcinogenic materials present, therefore, contact should be avoided.
3. Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis.
4. Entry of air into the apparatus while above 250°C may result in flash ignition of the volatile hydrocarbons, residue, or condensate. The potential exists for explosion of the hot vapours, with resulting hazards. Ensure no air is allowed to enter the apparatus while hot.

WASTE DISPOSAL:

1. Dispose of excess sample material in a manner appropriate to the sample.
2. Dispose of liquid condensate in a manner appropriate for potentially-carcinogenic materials.
3. Dispose of used sample vials in a manner appropriate for potentially-carcinogenic materials, considering the possible hazard of glass breakage and cuts.

APPARATUS, REAGENTS, AND MATERIALS:

1. Alcor Microcarbon Residue Tester, Model #100. Alcor Inc., San Antonio, Texas.
2. Hammond Constant Voltage Regulator, Model #CV2000 AFP. RAE Industrial Electronics, Edmonton, Alberta.
3. Nitrogen, oxygen-free: Matheson.
4. Nitrogen Gas Regulator.
5. 1/2 dram vial. Soda Glass: Alcor part #38060; Borosilicate Glass: Fisher part #03-340-2A.
6. 4 dram vial. Soda Glass: Alcor part #38061; Borosilicate Glass: Fisher part #03-340-2E.
7. Sample baskets for 1/2 dram vials: Alcor part #85335; 4 dram vials: Alcor part #85336.
8. Basket Lift Hook: Alcor part #85337.
9. Toluene for cleaning apparatus.
10. Analytical Balance with 0.1 mg sensitivity.

PROCEDURES:

Preparation of Reference Sample:

1. Monitoring of the performance of the system using a stable reference sample is vital to obtaining reliable results. Select a reference sample which is very stable by nature (not volatile or reactive), and as similar as possible to the bulk of the samples to be analyzed. The reference sample used by Syncrude is a topped product bitumen sampled in 1985. This material has an MCR of 14.39. A similar material may be available from the Alberta Research Council Sample Bank, but it may not be appropriate for a laboratory primarily analyzing very different samples.
2. In order to more easily monitor the performance of the microcarbon residue tester, a reference sample is analyzed each time samples are run. The reference sample, chosen to be as similar to the bulk of the samples as possible (1), is a Syncrude bitumen (Plant 7 product) sampled in 1985.
3. The reference sample is handled in an identical manner to the samples.

Sample Preparation:

1. Weigh a sample vial and record the weight to the nearest 0.1 mg.

   Note: Handle the vials with forceps during the weighing and filling steps to minimize weighing errors.
2. Stir the sample to be tested before subsampling. It may be necessary to warm the sample gently to reduce its viscosity. This can be accomplished by placing the sample container in a warm oven (70°C) for not more than 1.0 hours. Extremely viscous samples may be frozen with liquid nitrogen and shattered to provide suitably sized subsamples.

3. Viscous samples can be transferred to the vials using a wire rod and liquid samples using a disposable (Pasteur) pipet.
4. Determine the appropriate sample weight using the table below.

Expected % MCR	0.25	1.0	5	10	25
Weight sample (g)	10	2.5	0.5	0.25	0.1

5. Tare the vial and transfer the appropriate weight of sample to the vial. Record the weight to the nearest 0.1 mg.
6. Place the sample vials in the basket such that each tray contains 10 different samples and two quality control samples. Note the position of each sample with respect to the position numbers engraved on the basket top.

Operating Procedure:

1. Turn on the main power switch.
2. Turn on the nitrogen gas valve and adjust the pressure at the cylinder regulator to give a pressure of 20 psi on the instrument gauge.
3. Load the samples into the oven. Do not allow the sample basket to touch the oven wall or the thermocouple which protrudes through the oven wall.
4. Place the gravity seal lid on the oven.
5. Push PROG STATUS/SHIFT and hold, if display reads FLAG, push PROG/LOCAL-RESET to clear flag. Note that the instrument must be in LOCAL mode.
6. Ensure that the controller shows the program status as 4-1.
7. Push PROG/LOCAL-RESET once. The program light will come on indicating the controller is ready to run.
8. Hold the PROG-STATUS/SHIFT button and push the RUN button once. The run light will come on.
9. If the REMOTE HOLD and EVENT 1 lights are on, then push NITROGEN-ON switch to unlatch event 1.
10. Program will now run to its end which is 95 minutes.
11. At the end of the program, the EVENT 4 light will blink on and off. NOTE: The temperature in the oven must reach 250°C before it is SAFE to remove the gravity seal lid to ensure the residue does not oxidize.
12. The gravity seal lid can now be removed and placed over the fan vent for rapid cooling.
13. The sample basket should be placed in a desiccator until cool enough for weighing.
14. Each sample analysis is repeated in duplicate; duplicate analyses can only be obtained by repeating the entire analytical procedure.

CALCULATIONS: Calculate the % carbon residue as follows:

$$\%\ MCR = \frac{weight\ (residue + vial) - weight\ (vial)}{sample\ weight} \times 100$$

REPORT FORMAT: Report the duplicate values obtained as % microcarbon residue to the nearest 0.01.

PRECISION:

1. In general, the precision of this method is within the limits specified in ASTM D4530.
2. Any run for which the reference bitumen sample yields a result more than 2 standard deviations from its mean must be rejected and all the samples re-assayed.
3. The reference bitumen has an average MCR value of 14.39, with a standard deviation of 0.09.
4. The precision has been measured as:

   Average 10.39, standard deviation 0.079 with n = 22

   Average 13.0, standard deviation 0.073 with n = 20

   Average 14.32, standard deviation 0.072 with n = 30

   Average 15.94, standard deviation 0.101 with n = 36
5. Precision at lower levels has not been evaluated. Note that runs where the reference material did not meet criteria are rejected from the above data. Serious errors may go unnoticed without confirmation of the run by the reference material.

ACCURACY:

1. The arbitrary nature of the analysis precludes an accuracy statement. Note, however, that any solids in the sample will report as MCR, although they are not coke and should not be included in the result. Likewise any ash-forming material in the sample will report as MCR, but should not be included in the result. Thus the ash or solids should be determined and subtracted from the MCR result for samples containing these residues where these errors would be significant for the intended use of the data. A variation in MCR is observed as a function of residue weight. Maintenance of the residue within limits through adherence to the sample size table is required for accurate results.
2. Agreement between the two Syncrude laboratories was within 0.2% MCR at both 14.5 and 9.8% MCR.

TIME CONSIDERATIONS:

Time Per Analysis:	4 h
Technician Contact Time:	30 min
Samples Per Time Period:	10/d

REFERENCES: ASTM Method D4530, "Microcarbon Residue of Petroleum Products."

Determination of the Kinematic Viscosity of Transparent and Opaque Liquids

INTRODUCTION: Kinematic viscosity is a measure of the resistive force of a fluid under gravity. Many petroleum products are used as lubricants and the operation of equipment depends on the proper viscosity of the liquid. Thus, the accurate measurement of kinematic viscosity is essential for many product specifications. Also, the kinematic viscosity of many petroleum products is an important parameter for calculating the flow of the liquids through nozzles, orifices, and pipelines.

SCOPE: This method determines the kinematic viscosity of transparent and opaque petroleum products exhibiting the properties of a Newtonian liquid. The dynamic viscosity can also be calculated if the sample density is known.

SUMMARY: The time for a volume of liquid to flow through a marked zone in a calibrated glass capillary at a defined temperature is measured, and is directly related to the kinematic viscosity. Absolute kinematic viscosity values are obtained through comparison with standards of known viscosity.

SAFETY CONSIDERATIONS: Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis.

WASTE DISPOSAL: Dispose of excess sample materials in a suitable hydrocarbon storage tank.

APPARATUS, REAGENTS, AND MATERIALS:

1. CANNON-FENSKE routine viscometer (uncalibrated).
2. Two Sargeant-Welch constant temperature baths filled with high temperature oil set at 20 and 40°C. The baths must be capable of maintaining the temperature to within ±0.01°C:

   Sargeant-Welch Constant Temperature Baths, Model # 5-67429.
3. Two Sargeant-Welch Thermonitors for constant temperature control:

   Sargeant-Welch Thermonitor, Model # ST S-82052
4. Thermometers: Liquid-in-glass type with laboratory test certificate for corrections, accurate to within + 0.01°C.
5. Three GCA/Precision Scientific Timers accurate to 0.1 seconds.
6. Viscosity Standards - S-3, S-6, S-20, S-60, S-200, S-600, S-2000:

   Cannon Viscosity Standards

   P.O. Box 16

   State College, PA., USA 16804
7. Decon: for cleaning viscometer.

SAMPLE CONSIDERATIONS:

Amount Required:	50 mL
Destructive:	No
Properties:	The sample should contain no particulates or multiple phases and should not have volatile components at the measurement temperature.

PROCEDURE: Calibration:

Preparation of Calibration Standards:

The standards are used as purchased from Cannon.

Implementation of Standards:

1. Various size viscometer tubes are purchased from the factory and calibrated upon receipt.
2. The correct capillary size viscometer should be selected to match the viscosity range of the sample. The following table provides the ranges.

Recommended viscometer sizes for various viscosity ranges

Viscometer sizes	Viscometer constant C	Viscosity range
25	0.002	0.5–2
50	0.004	0.8–4
100	0.015	3–15
150	0.035	7–35
200	0.1	20–100
300	0.25	50–250
400	1.2	240–1200
500	8	1600–8000
600	20	4000–20000

3. The viscometer should be rinsed with toluene or other suitable solvent and dried by passing a slow stream of clean dry air through the viscometer. This should be done between successive determinations. Acetone should not be used as a cleaning solvent.
4. Periodically the viscometer should be cleaned with a chromic acid or decon solution to remove traces of organic deposits. Long periods of soaking in strong cleaning agents should be avoided. Recalibration of the viscometer should be performed after the use of strong cleaning agents.
5. From the following table select the tube size, the temperature at which the tube is to be calibrated, and the appropriate calibration standard.

Table for selecting tube size, temperature and calibration standard

Tube size	Temperature (degrees centigrade)		
	20	40	100
25	water	water	S3 or S6
50	water	S3	S6
100	S6	S6	S60
150	S6	S20	S200
200	S20	S60	S600 or S2000
300	S60	S200	S2000
400	S200	S600	–
500	S600	S2000	–
600	S2000	–	–

6. Record
   (a) tube size
   (b) temperature
   (c) viscosity of standard at this temperature.
7. Pour a small amount of standard into a small beaker.
8. Fill the tube with standard by inverting the tube, placing the small end into the standard and applying suction through the use of a 30-mL syringe on the other arm.
9. Attach viscosity tube holder and place into constant temperature bath.
10. Allow to stabilize for at least 15 minutes.
11. Attach syringe to the small end of tube. Draw up liquid into the lower bulb and past the top mark on the tube.
12. Allow the standard to flow down the tube, solely under the force of gravity.
13. Start the timer when the meniscus passes the top red etched line.
14. Stop the timer when the meniscus reaches the bottom red etched line.
15. Record the time.
16. Repeat six times. The times should differ by no greater than 0.5 seconds.
17. Average the flow times and calculate the constant for that tube as follows:

    $C = v / t$

    where: C = calibration constant (cSt/s)
    v = kinematic viscosity of standard (cSt)
    t = average flow times (s)
18. Use this constant when running samples with this tube at the calibration temperature.

SAMPLE ANALYSIS:

1. The viscometer, firmly mounted into a holder, is inverted with the small arm in the sample solution. Suction is applied to the large arm using a syringe. Enough sample is drawn to fill the two bulbs and reach the second etched mark.
2. Return the viscometer to the upright position and dry the outside of the small arm.
3. Place the viscometer into the oil bath with the top etched line about 2 cm below the surface of the bath oil.
4. Allow 15 minutes for the viscometer to reach the test temperature.
5. Apply an even and slow suction to the small arm to bring the sample a short distance above the top etched line.
6. The efflux time is determined by measuring the elapsed time required for the sample meniscus to pass from the top etched line to the bottom etched line under the force of gravity.
7. Repeat a second time and average the times. Check that the two times differ by no more than 0.5 seconds. If this cannot be achieved, closely check the sample for the presence of particulates or multiple phases. Reject the sample if present. If other samples behave in the same manner, clean and recalibrate the viscosity tube.
8. The kinematic viscosity is directly related to the efflux time.

CALCULATIONS:

1. Kinematic Viscosity:

   $v = C \times t$

   where: v = kinematic viscosity (cSt)
   C = calibration constant (cSt/sec)
   t = measured efflux time (sec)

2. Dynamic Viscosity:

   $n = v \times \rho$

   where: n = dynamic viscosity (cP)
   v = kinematic viscosity (cSt)
   ρ = density of sample (g/mL)

REPORT FORMAT:

1. The kinematic viscosity is reported in terms of centistokes (cSt) to the nearest 0.01. It is usual to report both of the duplicate results.
2. The dynamic viscosity is reported in terms of centipoises (cP) to the nearest 0.01.

PRECISION AND ACCURACY:

Precision:

The percent relative standard deviation should not exceed 0.35% more than one case in twenty for multiple measurements made on the same instrument by the sample operator (1). Results typically are in the range of 0.05% (% RSD).

Accuracy:

The accuracy of this analysis is maintained through the use of calibration standards. Calibration factors are produced for each of the viscometer tubes.

TIME CONSIDERATIONS:

Time Per Analysis:	20 min to 1 h
Technologist Contact Time:	20 min to 1 h
Samples Per Time Period:	1 to 3/h
Calibration Time:	1 h

REFERENCE:

ASTM Method D445, "Kinematic Viscosity of Transparent and Opaque Liquids."

Determination of Bromine Number for Liquid Petroleum Hydrocarbons by the Electrometric Method

INTRODUCTION: The bromine number is useful as a measure of aliphatic unsaturation in many of the upgrading streams. However, the magnitude of the bromine number is only an indication of the quantity of the bromine-reactive constituents and should not be taken as a true measure of olefinic unsaturation.

SCOPE: This method determines the bromine number of liquid petroleum hydrocarbons. The procedure is a modification of ASTM D1159 "Bromine Number of Petroleum Distillates and Commercial Olefins by Electrometric Titration."

SUMMARY: The sample is initially dissolved in a solvent consisting of glacial acetic acid, 1,1,1,-trichloroethane, methanol, and sulphuric acid. The solution is titrated with bromide-bromate titrant using dual platinum electrodes and a 10 μA polarizing current for end point detection.

BACKGROUND: Bromine number is defined as the number of grams of bromine consumed by 100 g of sample when reacted under specified conditions. The differences in procedure between Syncrude Research's bromine number determination and that of ASTM D1159 are:

a. A change in the equipment which retains the functional aspects of the specified equipment but which partially automates the analysis.

b. Whereas the ASTM method uses a 50 mV voltage change to identify the end point, the present method selects the inflection point of the titration curve. The latter end point is more easily obtained and more reproducibly defined.

SAFETY CONSIDERATIONS:

1. Acetic Acid: a skin and eye irritant. Flammable; flashpoint 43°C.
2. Potassium Bromide/Bromate Solution: avoid contact with skin. Toxic bromine vapours are generated when heated.
3. Sulphuric Acid: extremely corrosive.
4. 1,1,1-Trichloroethane: moderately toxic by inhalation and skin absorption. Contains inhibitor to prevent formation of phosgene on heating.
5. Methanol: flammable; flashpoint 12°C. May be fatal or cause blindness if swallowed or inhaled.
6. Cyclohexene: flammable; flashpoint –12°C. Moderately toxic by inhalation. Tolerance 300 ppm in air.
7. Hydrochloric Acid: liquid burns eyes and skin; vapour irritates respiratory system. Handle with caution.
8. Liquid waste: place all liquid wastes in a designated clearly labelled container. Arrangements for final disposal should be made with the Chemical Safety Advisor.

APPARATUS, REAGENTS, AND MATERIALS:

1. pH meter: with millivolt scale, 10 amp polarizing current output, and recorder output.
2. Dual platinum electrodes.
3. Potentimetric recorder: with appropriate scale to record the meter output with 0 to –1000 mV input to the pH meter.
4. Autoburette: Radiometer ABU 12 or ABU 13 fitted with a 25 mL burette. Radiometer A/S Emdrupvej 72, DK-2400 Copenhagen NV, Denmark.
5. Timer: repeat cycle, set to trigger the ABU 12 at 30 seconds intervals. See Figure 1 for electrical connections and timer design. To adjust the microswitch, set the ABU 12 to a speed of 40 with INCREMENTS off. Zero the volume counter, turn the timer on, and observe the volume counter before and after the microswitch has been activated. Adjust the microswitch for an addition of 0.04 to 0.07 mL per switch closure.
6. Magnetic stirrer and stirring bar.
7. Volumetric flasks: 250 and 1000 mL, Class A.
8. Beaker: 250 mL.
9. Iodine flask: 500 mL.
10. Ice bath.
11. Reagents (all C.S.A. reagent grade where available).
    - Acetic acid, glacial,
    - Arrowroot starch,
    - Cyclohexene, purified,
    - Methanol,
    - Potassium bromate,
    - Potassium bromide,
    - Potassium iodide,
    - Sulphuric acid,

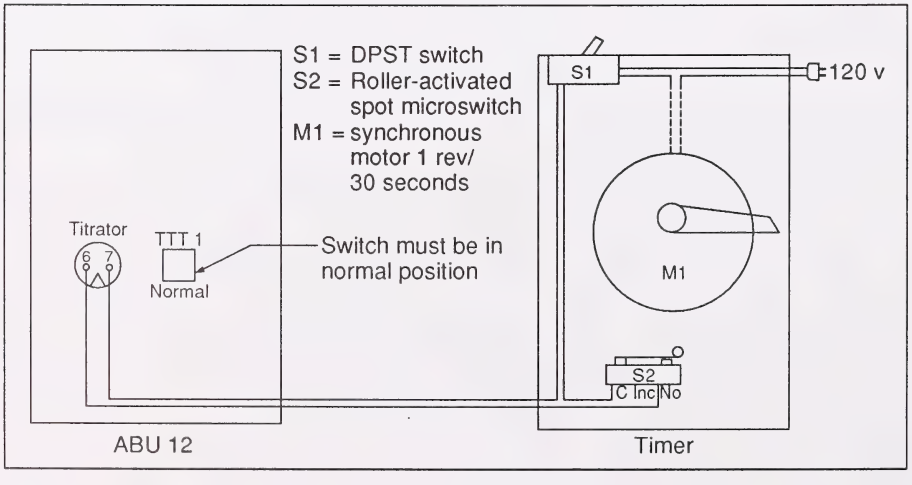

Figure 1. Time and electrical connections for the automated bromine number apparatus.

- Hydrochloric acid,
- 1,1,1-Trichloroethane.

12. Standard solution: certified 0.1 N sodium thiosulphate solution, Fisher #SS368-1.
13. Analytical balance.
14. De-ionized water.

SAMPLE CONSIDERATIONS:

Amount Required:	10 mL
Destructive:	Yes
Properties:	Petroleum distillates that have an IBP above –12°C and a 90% distillation point under 327°C.

INTERFERENCES:

When the bromine number is taken as a measure of bromine-reactive constituents under specified reaction conditions, the analysis is interference-free. However, this is not the case if bromine number is taken as a measure of olefinic unsaturation. The data provided by ASTM D1159 illustrate this point (1) and should be consulted before interpreting results. The presence of H_2S and other reactive sulphur species interfere with this analysis.

PROCEDURES:

Calibration:

Preparation of Standards:

1. Prepare a nominal 0.50 N potassium bromide-bromate solution by dissolving 13.92 g of potassium bromate and 51.0 g of potassium bromide, both previously dried at 105°C for 30 minutes, in distilled water and diluting to 1000 mL.
2. A starch indicator solution is prepared by mixing 1.25 g arrowroot starch with a few millilitres of hot distilled water to form a paste. Add the paste to 500 mL of boiling distilled water. Allow to cool and decant into a stopper bottle. This solution has a short shelf life, e.g., 2–3 days.
3. Dissolve 150 g potassium iodide in distilled water and dilute to 1000 mL. Prepare this solution at least every two months.
4. A titration solvent is prepared by mixing 1428 mL of glacial acetic acid, 268 mL of 1,1,1-trichloroethane, 268 mL of methanol, and 36 mL of 1:5 sulphuric acid.
5. Standardize the potassium bromide-bromate solution every two weeks. Place 50 mL of glacial acetic acid and 1 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) in a 500-mL iodine number flask. Chill the solution in an ice bath for approximately 10 minutes and, with constant swirling of the flask, add from the autoburette 5 ± 0.01 mL of bromide-bromate solution at the rate of one or two drops per second. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 mL of KI solution in the flask. After five minutes remove the flask from the ice bath and allow the KI solution to flow into the flask by slowly removing the stopper. Shake vigorously, add 100 mL of water in such a manner as to rinse the stopper, lip, and walls of the flask, and titrate promptly with 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solution. Near the end of the titration, add 1 mL of starch indicator solution and titrate slowly to disappearance of the blue colour.

STANDARD CHECK:

1. Cyclohexene should be used as a check whenever new standards solutions are prepared.
2. Place 10 mL of toluene in a 50-mL volumetric flask. Add 0.6 to 1.0 g of cyclohexene determined to 0.001 g. Dilute to volume with toluene. Pipet a 5-mL aliquot of the cyclohexene solution into 100 mL of titration solvent. Place in an ice bath.
3. Set the titration vessel and ice bath on the titration stand, insert the platinum electrodes, start the stirrer and allow the system to equilibrate. The pH meter and recorder will indicate –1000 to –1400 mV.
4. Refill the Autoburette with titrant, zero the volume counter, and set INCREMENTS on at a titration speed of 40. Turn on the cycle timer and recorder. The system will now make 0.10-mL additions at 30-second intervals until the titration is stopped. The recorder will monitor the progress of the titration. Occasionally during the titration, the recorder output should be marked with the accumulated volume of titrant indicated by the Autoburette volume counter.
5. When the titration is complete, turn off the Autoburette, recorder, timer and magnetic stirrer.

SAMPLES:

Bromine Number versus Sample Size

Bromine number	Sample size (g)
0–10	5 to 4
11–20	2 to 1.6
21–50	1 to 0.8
51–100	0.5 to 0.4
> 100	0.2 to 0.1

1. The weight of the sample should be determined to 0.001 g. For samples of high bromine number it is best to weigh 10 times the amount of sample specified in the above table, dilute to 50 mL with toluene, and then use a 5-mL aliquot for the bromine number.
2. Add 100 mL of titration solvent. If the hydrocarbon sample separates to form a two-phase system, add toluene up to 40 parts of toluene for one part of sample, to render the sample soluble. If the sample does not remain dissolved during the titration the results will be invalid. Highly volatile samples must be cooled in an ice bath before titration. Refill the Autoburette with titrant, zero the volume counter, and set INCREMENTS on at a titration speed of 40.
3. Set the titration vessel on the titration stand, insert the platinum electrodes, start the stirrer, and allow the system to equilibrate. The pH meter and recorder will indicate –1000 to –1400 mV for a typical sample.
4. Turn on the cycle timer and recorder. The system will now make 0.10 mL additions at 30-second intervals until the titration is stopped. The recorder will monitor the progress of the titration. Occasionally during the titration the recorder output should be marked with the accumulated volume of titrant indicated by the Autoburette volume counter.

5. When the titration is complete, turn off the Autoburette, recorder, timer, and magnetic stirrer.

Determination of End Point:

The equivalence point is found by fitting the titration curve with a straight line in the region of its inflection point and bisecting the line between the points where the titration curve deviates from the straight line. The point of bisection is taken as the equivalence point. The volume delivered at the equivalence point is calculated by linearly interpolating between the titrant volume markings on the recorder trace.

Blanks:

Titration blanks using solvent only must be run periodically once a day. Due to the low blank values which typically occur, e.g., 0.1 to 0.2 mL, use of the Autoburette in the manual mode is recommended.

CALCULATIONS:

Calculate the bromine number of the sample as:

$$\text{Bromine number} = \frac{7.99\ N\ (A - B)}{W}$$

where A = volume of titrant required for the sample, mL
B = volume of titrant required for the blank, mL
N = normality of titrant
W = sample weight, g

REPORT FORMAT:

Report as bromine number to the nearest whole number.

PRECISION AND ACCURACY:

1. The ASTM D1159 criteria for repeatability are used to judge the acceptability of data from the present method.
2. Cyclohexene: the mean bromine number obtained is 186 ± 4.8 (ls).

TIME CONSIDERATIONS:

Time Per Analysis:	45 min
Technologist Contact Time:	20 min
Samples Per Time Period:	8/d
Calibration Time:	30 min
Standardization Time:	1 d

REFERENCES:

1. ASTM Method D1159, "Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration."
2. UOP, "Bromine Number of Petroleum Distillates and Bromine Index of Industrial Aromatic Hydrocarbons," UOP Laboratory Test Methods for Petroleum and its Products, Universal Oil Products Co., Des Plaines, IL.

Supercritical Fluid Chromatography Analysis of Aromatic Content of Petroleum Products

SCOPE: This method determines the weight-percent of aromatic compounds in petroleum products. The method is limited to naphtha and light gas oil samples. It is also limited to samples having a vapour pressure sufficiently low to permit sampling at ambient temperatures.

SUMMARY:

1. The sample is injected into a supercritical fluid chromatograph (SFC), equipped with a column of limited efficiency, which separates the hydrocarbons into saturated (non-aromatic) and aromatic compounds.
2. Due to its similar response to both saturated and aromatic compounds, a flame ionization detector (FID) is used to detect the components.
3. At constant pressure and temperature, the area under the chromatogram is measured as a function of retention time. The accumulated area is normalized to 100% to allow calculation of the percent of the total sample which is aromatic. The assumptions made are:
   a. all of the components in the samples of interest will elute from the column in the time allowed.
   b. any peak which is detected with a retention time shorter than the saturated components is assumed to be baseline noise.
   c. the relative response factor of the detector for each component in the sample mixture is one.
4. For naphtha and light gas oil samples these assumptions should be compatible with ASTM D2549.
5. A report of area percent versus retention time is automatically generated. The total area is corrected for any areas observed with retention times shorter than the saturated components, and the area percent values for the remaining peaks are corrected accordingly. The area percent values for the saturated components are combined, and the area percent values for the aromatic components are combined.

SAFETY CONSIDERATIONS:

1. Caution should be used when handling compressed gas cylinders.
2. Carbon dioxide: liquid at –37°C, contact with skin may cause "burns."
3. Carbon disulphide: extremely flammable; flash point –30°C. Highly toxic, tolerance 10 ppm in air. Liquid is absorbed by skin, avoid contact.
4. Hydrogen is a highly explosive gas. All transfer lines and cylinder connections should be checked for leaks periodically. The gas supply to the FID should be turned off whenever there is not a column connected to the detector.
5. Care should be exercised when handling hydrocarbons.
6. The SFC instrument has an upper pressure limit of 400 atmospheres (40,000 kPa). This should never be exceeded.

WASTE DISPOSAL: All sample materials should be disposed of in a suitable hydrocarbon storage tank.

APPARATUS, REAGENTS, AND MATERIALS:

1. Lee Scientific Series 600 Supercritical Fluid Chromatograph with an AST Premium 386 SX personal computer running Dionex's ACI 600 chromatography software (v2.2 or higher) and a NEC P5200 printer.
2. Flame ionization detector.
3. Column, two in series, 1 mm x 25 cm, 5-µm silica (Applied Biosystems Brownlee columns).
4. SFC grade carbon dioxide (Scott Specialty Gases).
5. Hydrogen, zero grade, Matheson.
6. Air, zero grade, Matheson.
7. Syringe: 50 microlitre, with 2" 22-gauge needle, Hamilton #705SNR (Chromatographic Specialties #80565).
8. Disposable, crimp-top vials 1 mL: HP #5081-8721.
9. Crimp seals (Teflon-faced neoprene): HP #5080-8713.
10. Crimper for 1 mL vials.
11. Standard, 8.5" x 11", tractor-feed printer paper.
12. Disposable Pasteur pipets and bulbs.
13. Soap bubble flowmeter.
14. Stop watch.

SAMPLE CONSIDERATIONS:

Amount Required:	This analysis requires 12 drops of a light gas oil sample or eight drops of a naphtha sample.
Properties:	This method is applicable to light gas oil and naphtha samples.
Destructive:	Yes

PROCEDURES:

Instrument Set-Up:

1. Ensure that the carrier carbon dioxide is flowing and the pressure is between 75 and 160 atmospheres.
2. Turn on the FID air (50 psi, 300 mL/min) and the FID hydrogen (25 psi, 30 mL/min) and ignite the flame.
3. Set the following instrument parameters:

   DET TEMP: 250°C

   INJ TEMP: 25°C

   ATTN: 6

   RANGE: 1

   SIGNAL: A

   OVEN TEMP: 35°C

   PUMP PRESSURE: 160 atmospheres

   RUN TIME: 8 min (Naphtha Samples)

   RUN TIME: 10 min (Light Gas Oil Samples)
4. These conditions can be properly set, from the Dionex Run program, by loading NAPH160.MET for naphtha samples, or LGO160.MET for light gas oil samples.

Column Conditioning:

1. All new columns must be conditioned before use.
2. The column is connected to both the injector and detector of the SFC.
3. The oven temperature is set to 35°C and the pump pressure is set to 200 atmospheres.
4. The column is kept at these conditions until the FID signal stabilizes at some value less than 50 pA.

Preparation of Samples:

1. The preparation of samples is straightforward. To minimize the loss of light ends, samples should be analyzed promptly after submission.
2. For naphtha samples, place approximately eight drops into an auto sampler vial. The sample vial is then brought to volume with carbon disulphide.
3. For light gas oil samples, place approximately 12 drops into an auto sampler vial. The sample vial is then brought to volume with carbon disulphide.

Analysis of Samples:

1. In the Dionex Run program the appropriate method (NAPH160.MET for naphthas or LGO160.MET for light gas oils) is loaded and initialized.
2. The injection valve is rinsed a minimum of three times with 50 microlitre volumes of the sample to be analyzed.
3. A 50-µL volume of the sample is loaded into the injection valve, and the syringe needle is left in the injection port.
4. RUN is clicked in the dialogue box of the Dionex software, and the syringe is removed from the injection port.
5. After completion of the chromatogram, the report is automatically generated and the instrument is ready to be initialized for another injection.

CALCULATIONS:

1. Any area % values with retention times shorter than 4.0 minutes are considered to be baseline noise and are subtracted from the total chromatographic area %.
2. The area % values for the remaining peaks (t_R > 3.99 minutes) are normalized to a total of 100%.
3. The corrected area % values for the saturated components (t_R 4.0–4.5 minutes) are combined and represent the % by mass of the sample which are saturated compounds.
4. The corrected area % values for the aromatic components (t_R > 4.5 minutes) are combined and represent the % by mass of the sample which are aromatic compounds.

REPORT FORMAT:

The report consists of two values:

a. the weight % of the sample which is saturated compounds;
b. the weight % of the sample which is aromatic compounds.

TIME CONSIDERATIONS:

Time Per Analysis:	10 min (naphtha) or 12 min (light gas oil)
Technologist Contact Time:	5 min
Samples Per Time Period:	30/8 h technologist shift (naphtha) or 25/8 h technologist shift (light gas oil).

PRECISION: Precision evaluations of the repeatability of the analyses have been carried out using two samples. The results are summarized in the following tables.

Stream 221027 Naphtha
March 22, 1991 – April 5, 1991

Component	Number of determinations	Mean	1 STD Dev.	2 STD Dev.	Highest value	Lowest value
Saturates	10	91.58	0.30	0.60	92.17	91.19
Aromatics	10	8.42	0.30	0.60	8.81	7.83

2HPP Light Gas Oil
March 22, 1991 – April 5, 1991

Component	Number of determinations	Mean	1 STD Dev.	2 STD Dev.	Highest value	Lowest value
Saturates	10	59.13	0.45	0.90	59.76	58.33
Aromatics	10	40.87	0.45	0.90	41.67	40.24

4

DISTILLATION

Simulated Distillation of Petroleum Products

INTRODUCTION: The boiling range distribution of petroleum products may be determined using a true distillation which is both manpower- and time-intensive or by utilization of a simulated distillation procedure. The use of simulated distillation allows for minimal sample consumption and rapid generation of data.

SCOPE:

1. This method is an implementation of ASTM D2887. The method is limited to samples with a boiling range of at least 50°C and a final boiling point less than 535°C.
2. It is also limited to samples having a vapour pressure sufficiently low to permit sampling at ambient temperatures.

SUMMARY:

1. The sample is injected into a gas chromatographic column of limited efficiency which separates hydrocarbons in boiling point order. The column should provide a resolution of at least 3 and not more than 8.
2. The flame ionization detector used for simulated distillation is equipped with a jet having an inside diameter of 0.030 inch, rather than the usual 0.018 inch size. This larger jet reduces the severity of jet clogging due to column bleed, which can be substantial at the high temperatures required for a full-range simulated distillation analysis.
3. The large jet causes about a 30% loss in sensitivity relative to the standard jet. Simulated distillation does not require high sensitivity so the trade-off, in favour of easier maintenance, is justified.
4. While the column temperature is programmed up at a reproducible rate, the area under the chromatogram is measured as a function of time. The accumulated area is normalized to 100% to allow calculation of percent recovered at a given time. The time axis is converted to boiling point using a calibration curve obtained, under the same chromatographic conditions, by analyzing a known mixture of *n*-paraffins covering the boiling range expected in the sample. The assumptions made are:
   a. All of the components in the samples of interest will be separated by the chromatographic column in boiling point order, i.e., that they will behave as *n*-paraffins.
   b. The relative response factor of the detector for each component in the sample mixture is one.
5. Neither assumption is strictly true; however, both are totally compatible with ASTM D2887.
6. A report of percent recovered versus boiling point in °C is automatically generated. The initial boiling point is defined as the point at which a cumulative area count equal to 0.5% of the total area under the chromatogram is obtained. Similarly, the final boiling point is defined as the point at which a cumulative area count equal to 99.5% of the total area under the chromatogram is obtained.

BACKGROUND: The boiling range distribution of many of Syncrude's upgrading streams is monitored routinely. The information is of use in evaluating fractionator performance, correct product routing, and ultimately in determining the potential ability to generate specific fuel oils from synthetic crude oil

SAFETY CONSIDERATIONS:

1. Caution should be used when handling compressed gas cylinders.
2. Carbon dioxide: liquid at –37°C, contact with skin may cause "burns."
3. Carbon disulphide: extremely flammable; flashpoint –30°C. Highly toxic; tolerance 10 ppm in air. Liquid is absorbed by skin. Avoid contact.
4. Care should be exercised when handling hydrocarbons.

APPARATUS, REAGENTS, AND MATERIALS:

1. Hewlett Packard Gas Chromatograph #5880 with 5880A series GC terminal and alphanumeric keyboard.
2. Hewlett Packard Simulated Distillation Software for S880.
3. Flame ionization detector with 0.030 inch FID JET: HP #19301-80610.
4. Injection port septa: HP #5080-6721.
5. Column, 1/8" x 20" 10% VCW-W982 on 80/100 mesh chrom, P-AW: HP #19006-60028.
6. Hewlett Packard 7673A Automatic Sampler.
7. Hewlett Packard Reference Gas Oil.
8. Analytical Standard Kit #211CX, #2GICX (C_6–C_{40}) from Polyscience.
9. *n*-Tetratetracontane (C_{44}): #4-8218 from Supelco.
10. Propane, instrument grade, lecture bottle, Matheson.
11. *n*-Butane, instrument grade, lecture bottle, Matheson.
12. Plant 13 naphtha, obtained from Mildred Lake.
13. Hydrotreated Gas Oil, obtained from Mildred Lake (Plant 15 product).
14. Carbon disulphide.
15. Analytical balance.
16. Syringe 10 μL: HP #9301-0021.
17. Disposable crimp top vials 1 mL: HP #5081-8721.
18. Crimp seals (Teflon faced neoprene): HP #5080-8713.
19. Crimper for 1 mL vials.
20. 50 mL serum vials: Supelco #3-3109.
21. Crimp seals (standard): Supelco #3-3250.
22. Septa for crimp seals (Neoprene): Supelco #3-3203.
23. Crimper for 50 mL vials.
24. Thermal printer paper: HP #5080-8778.
25. Disposable Pasteur pipettes and bulbs.
26. Helium high purity (HP), Matheson.
27. Hydrogen, zero grade, Matheson.
28. Air, zero grade, Matheson.
29. Supelco carrier gas purifier: Supelco #2-3880.
30. Replacement tubes for above: Supelco #2-2398.
31. Soap bubble flowmeter.
32. Stop watch.

SAMPLE CONSIDERATIONS:

Amount Required: This analysis requires approximately 2 mL of liquid sample.

Properties: The final boiling point of the liquid must be less than 535°C.

Destructive: Yes

PROCEDURES: Instrument Set-Up:

1. Ensure that the helium carrier gas is flowing. The carrier gas flowrate is set at 33 mL/min with the oven temperature set at 50°C.
2. Replace septum with a new pre-baked septum if necessary.
3. Turn on both the FID air (400 mL/min) and the FID hydrogen (30 mL/min) and ignite the flame.
4. Set the following instrument parameters:

DETl TEMP: 360°C

INJl TEMP: 350°C

ATTN: 10

%OFFSET: 10

SIGNAL: A

OVEN TEMP	INITIAL TIME	0.00 min
OVEN TEMP	INITIAL VALUE	–40°C
OVEN TEMP	PRGM RATE	10.00°C min
OVEN TEMP	FINAL TIME	10.00 min
OVEN TEMP	FINAL VALUE	350°C
OVEN TEMP	POST TIME	0.00 min
EQUILIBRATION TIME		3.00 min
OVEN TEMP LIMIT		405°C
DET 1 TEMP LIMIT		405°C

Column Conditioning:

5. All new columns must be conditioned before use.
6. Connect the column to the injector; do not connect to the detector.
7. Cap detector inlet to prevent detector gases from entering oven.
8. With the oven at room temperature, purge the column thoroughly with helium carrier gas flowing at 25 mL/min; 30 min should be sufficient.
9. Turn the carrier gas off.
10. Raise the oven temperature to the maximum operating temperature (350°C) and hold for two hours with no flow through the column.
11. Cool the oven down to 80°C, then turn the carrier flow on.
12. Program the oven up to the maximum temperature three times with the carrier flow on.
    a. Initial oven temperature –40°C
    b. Final oven temperature 350°C
    c. Program rate 10°/min
13. Connect the column to the detector.
14. Test for leaks at room temperature. If none is found, the column should be ready for use. Program the oven up to the maximum temperature and observe the resultant baseline.

Standard Preparation:

15. The simulated distillation method depends upon construction of a calibration curve for the gas chromatographic system. This calibration curve relates boiling points of known species to their respective retention times. The standard required is made up of:

Carbon #	Name
C44	*n*-tetratetracontane
C40	*n*-tetracontane
C38	*n*-octatriacontane
C36	*n*-hexatriacontane
C32	*n*-dotriacontane
C30	*n*-triacontane
C28	*n*-octacosane
C26	*n*-hexacosane
C25	*n*-pentacosane
C24	*n*-tetracosane
C23	*n*-tricosane
C22	*n*-docosane
C21	*n*-heneicosane
C20	*n*-eicosane
C19	*n*-nonadecane
C18	*n*-octadecane
C16	*n*-hexadecane
C14	*n*-tetradecane
C12	*n*-dodecane
C11	*n*-undecane
C10	*n*-decane
C9	*n*-nonane
C8	*n*-octane
C6	*n*-hexane
C5	*n*-pentane
*C4	*n*-butane
*C3	propane

* 2 mL each to be added just prior to the run.

16. Prepare the standard by adding approximately 0.5 g of each of the paraffinic hydrocarbons listed above to about 40 mL of carbon disulphide.
17. Transfer about 1 mL volumes of the standard solution to 2-dram vials. Add about 2 mL of *n*-butane and propane to the vial just prior to use.

Preparation of Samples:

18. The preparation of samples is quite straightforward. Samples should be analyzed promptly after submission to minimize loss of light ends.
19. Place approximately 1 mL of sample into an auto sampler vial. If the sample is too viscous to allow proper syringe injection, then the sample must be diluted slightly with carbon disulphide. The usual dilution ratio is 1:4; sample: carbon disulphide.

Preparation of Reference Samples:

20. In order to more easily monitor the performance of the simulated distillation package, several reference samples are analyzed each time

samples are run. In general two reference samples are used:

- Plant 13 Naphtha
- Plant 15 Gas Oil

21. Both samples are obtained in relatively large quantities from the Mildred Lake site and transported to Edmonton. Upon arrival the samples are re-bottled into crimp seal autosampler vials
    - The Plant 13 Naphtha is re-bottled neat.
    - The Plant 15 Gas Oil is diluted 1:4 (Gas Oil:CS_2) and re-bottled.
22. The carefully labelled bottles are stored under refrigeration until used. Any excess can be stored in the cooler.

Analysis of Samples:

23. Prepare calibration mixture, samples, and carbon disulphide wash bottle.
24. Load sample tray.
25. Bring the oven temperature up to 350°C for approximately five minutes.
26. Bring the oven temperature to about 40°C and carry out a column compensation run.
27. Answer dialogue questions as asked, depressing "ENTER" after each answer.
28. Using the auto sequence dialogue, enter the position of the wash bottle.
29. Identify each sample in the sample table.
30. After 3 µL of the calibration blend has been injected, reset the syringe stop to allow for 1-µL injections of sample. All calculations are carried out automatically.

CALCULATIONS:

1. While the column temperature is programmed up at a reproducible rate, the area under the chromatogram is measured as a function of time. The accumulated area is normalized to 100% to allow calculation of percent recovered at a given time. The time axis is converted to boiling point using a calibration curve obtained, under the same chromatographic conditions, by analyzing a known mixture of *n*-paraffins covering the boiling range expected in the sample.
2. The initial boiling point is defined as the point at which a cumulative area count equal to 0.5% of the total area under the chromatogram is obtained. Similarly, the final boiling point is defined as the point at which a cumulative area count equal to 99.5% of the total area under the chromatogram is obtained.

REPORT FORMAT:

A report of percentage recovered to the nearest 0.1% versus boiling point in °C is automatically generated.

TIME CONSIDERATIONS:

Time Per Analysis:	1 h
Technologist Contact Time:	15 min
Samples Per Time Period:	18 per 24-h day
Calibration Time	1 h

PRECISION: Precision evaluations of the repeatability of the distillation curves have been carried out using two different samples. The results are summarized in Tables 1 and 2.

REFERENCES: ASTM Method D2887, "Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography."

Table 1. Plant 13 Naphtha
January 16, 1984–November 15, 1984

% Off	# of points	Mean	1 Std dev.	2 Std dev.	Highest value	Lowest value
IBP	80	–12.0	3.38	6.76	–2.7	–18.2
5	80	34.9	2.51	5.01	47.0	31.2
10	80	66.5	1.82	3.63	72.4	61.9
30	80	131.5	2.62	5.24	141.7	126.5
50	80	174.5	1.51	3.02	180.4	171.3
70	80	204.1	1.25	2.49	208.6	201.5
90	80	235.4	0.92	1.85	237.6	233.6
95	80	249.5	1.04	2.08	251.7	245.7
FBP	80	295.0	3.87	7.73	306.2	287.9

Table 2. Plant 15 Gas Oil
January 16, 1984–November 21, 1985

% Off	# of points	Mean	1 Std dev.	2 Std dev.	Highest value	Lowest value
IBP	128	204.5	1.05	2.09	206.7	202.4
5	128	235.0	0.87	1.83	237.1	231.1
10	128	252.8	0.84	1.69	255.0	250.4
30	128	302.3	1.05	2.10	304.7	300.1
50	128	345.4	1.38	2.75	348.4	340.9
70	128	392.3	1.76	3.53	396.0	390.0
90	128	456.0	2.21	4.41	460.6	452.0
95	128	483.4	2.63	5.27	488.5	477.5
FBP	128	539.8	6.06	12.11	554.5	519.7

The Spinning Band Distillation of Liquid Hydrocarbons and Bitumen

INTRODUCTION: Distillation is one of the simplest methods used to separate complex mixtures of petroleum samples. The Spinning Band Method employs a rotating metal band inside the distillation column. The principles and advantages of the Spinning Band method are documented elsewhere (1,2).

SCOPE: The samples covered by this method include liquid hydrocarbon mixtures and bitumens. For liquid hydrocarbons, the Initial Boiling Point (I.B.P.) should exceed room temperature at atmospheric pressure. The distillation is terminated at an atmospheric equivalent temperature of 524°C. For bitumen samples the distillation is terminated at a pot temperature of 360°C.

SUMMARY: Samples are distilled under atmospheric and reduced pressures of 2.67 kPa and 80 Pa (20.0 and 0.60 mm Hg) in a distillation unit equipped with a spinning band column. The spinning band provides a large contact area between the liquid and vapour phases, thereby increasing the number of theoretical plates in the column and thus its fractionating efficiency. Readings of vapour temperature, which is convertible to atmospheric equivalent temperature, and distillate volume, which is convertible to volume percent, are used to plot a distillation curve. Distillate yields for naphtha, light gas oil, heavy gas oil, and residue fractions are determined on a gravimetric basis.

BACKGROUND: Distillation is one of the simplest methods to separate the complex mixtures in petroleum samples. ASTM and UOP include several types of distillation for application to diverse sample materials:

ASTM D 86	Distillation of Petroleum Products
ASTM D 216	Distillation of Natural Gasoline
ASTM D 285	Distillation of Crude Petroleum
ASTM D 1160	Distillation of Petroleum Products at Reduced Pressure
ASTM D 2892	Distillation of Crude Petroleum (15 Theoretical Plate Column)
UOP 1	Distillation of Heavy Petroleum Oils
UOP 76	High-Vacuum Distillation of High Boiling Range Petroleum Products
UOP 77	Crude Oil Evaluation by Hempel Distillation
UOP 79	Fractionation of Petroleum Distillates and Crude Oils
UOP 109	Vacuum Distillation of Topped Crude Oils and Similar Petroleum Products

By using the Spinning Band method, samples can be distilled under atmospheric or reduced pressure. For each twofold pressure reduction the boiling point of most compounds is lowered by approximately 15°C. Some components present in bitumen are thermally unstable and crack at temperatures below their boiling points. To avoid cracking, the pressure is reduced during the distillation. However, due to the pressure drop between the still head and the McLeod gauge, the lowest pressure used in this procedure is 80 Pa (0.6 mm Hg). This corresponds to an atmospheric equivalent temperature (AET) of approximately 500°C for bitumen samples.

The samples are distilled into a number of fractions so that further analyses can be performed on the cuts. The designations and boiling point ranges employed are:

Naphtha	IBP–195°C
Light Gas Oil	195–343°C
Heavy Gas Oil	343–524°C
Residue	>524°C

where IBP is the initial boiling point.

The Sydney Young equation is used to relate vapour temperature to atmospheric equivalent temperature (AET) for distillation at atmospheric pressure (2). For distillation at reduced pressure, an equation based on the data of Maxwell and Bonnell is used (3,4). The effect of hydrocarbon type (5), as measured by the UOP characterization factor, K, is included in the latter calculation. A value for this factor of 12.5 or higher indicates a material predominately paraffinic in nature, whereas highly aromatic materials have a value of 10 or less. The calculations for this method employ a K-factor of 11.1, which has been found suitable for Athabasca bitumen.

INTERFERENCES:

Water contained by liquid hydrocarbon samples in either dispersed or coalesced form will cause severe bumping during the distillation. Solids present in a sample will report to the residue fraction and consequently bias distillate yields. Therefore, most of the water and solids must be removed as outlined in the sample preparation step of this procedure.

SAFETY CONSIDERATIONS:

1. Dry ice: freezes skin, wear protective gloves.
2. Liquid nitrogen: freezes skin, wear protective gloves.
3. Isopropyl alcohol: irritant to the skin and respiratory tract. Highly flammable.
4. Toluene: moderately toxic by skin absorption and inhalation. Possesses irritant and anaesthetic properties. Highly flammable.
5. Glassware under reduced pressure is capable of violent implosion. Break vacuum with extreme caution.
6. Do not use liquid nitrogen in the dry ice traps.

APPARATUS, REAGENTS, AND MATERIALS:

1. Adiabatic metal mesh spinning band still: 480 mm x 7 mm ID column, 40 theoretical plates, 0.3 mL hold-up, vacuum capability to 4.0 Pa (0.03 mm Hg), monel band, 29 rev/s motor and direct drive system: Perkin-Elmer order number 086-0901. The manual reflux valve assembly is replaced by the auto-reflux valve assembly: Perkin-Elmer order numbers 086-0215 and 086-0213.
2. Still pots: 500 mL for liquid hydrocarbon samples, 200 mL for bitumen samples, 50 mL for still hold-up. Single neck, round bottom flasks to fit the column and equipped with thermocouple well: Perkin-Elmer order numbers 086-0916, 086-0232, and 086-0230, respectively. Rubber stoppers to fit above flasks are also required.
3. Fraction cutter and supply of 25 mL capacity receivers: Perkin-Elmer order numbers 086-0313 and 086-0314, respectively. Glass stoppers to fit the receivers are also required.
4. Vacuum gauge: Universal 3-scale McLeod type, portable, VWR No.

31704-008, Western Scientific Services Ltd., 2520 Simpson Road, Richmond, B.C. V6X 2P9.

5. Heating mantle: 270 W, to fit 500 mL and 200 mL round bottom flasks. Top heating mantles: 170 W, to fit the flasks.
6. Heating tape: 8 x 300 mm. The heating tape is supplied as part number 519663 by Dohrmann Division of Envirotech Corp., 3240 Scott Boulevard, Santa Clara CA 95050 is suitable.
7. Variable transformers for heating mantles and heating tape.
8. Magnetic stirrer with bar.
9. Indicator control panel equipped with multipoint temperature selector, digital temperature indicator and reflux timer. The timer requires a minimum ON or OFF setting of one second. The Flexopulse Model HG92 supplied by Eagle Signal, 736 Federal, Davenport, IA 52803 is suitable.
10. Two vacuum pumps and tubing: the primary vacuum pump requires 8.3 L/s free air capacity.
11. Pinch clamp: no. 28.
12. Surge tank, manifold, mineral oil trap, dry ice traps, and needle valve as illusted schematically in Figures 1 to 3.
13. Centrifuge: 87 rev/s max., 4275 x G, 6 x 1000 mL capacity, complying with class 1 Group D explosion-proof requirements, equipped with a six-place horizontal head and 250 mL aluminum cups.
14. Balances:

    Top loading to 0.001 g, 320 g capacity

    Top loading to 0.01 g, 1200 g capacity.
15. Barometer: U.S. Signal Corps type.
16. Dewar flask: 10 L, for liquid nitrogen.
17. Evaporating dish: 120 mL, porcelain.
18. Separatory funnel: 500 mL.
19. Apiezon T grease.
20. Reagents:

    Dry ice

    Isopropyl alcohol, A.C.S. reagent grade

    Liquid nitrogen

    Mineral oil

    Nitrogen gas

    Toluene, A.C.S. reagent grade.
21. Molecular sieves – type 4A.

PROCEDURES: Sample Preparation: Liquid Hydrocarbon Samples:

1. Liquid hydrocarbon samples may contain water. Centrifuge these samples at 33 rev/s for 30 minutes to separate the major portion of the water from the hydrocarbon phase. Carefully withdraw the hydrocarbon phase by means of a syringe and transfer to a 500 mL separatory funnel containing approximately 60 g of molecular sieve. Allow to stand overnight.
2. Weigh the still pot containing a magnetic stirring bar and fitted with a rubber stopper on a top loading balance to the nearest 0.01 g.

Discarding the first few drops which may contain water, collect approximately 100 mL of sample in the still pot. Stopper and re-weigh. Take a small portion of the sample remaining in the separatory funnel and determine its density at 20°C using Method 3.3.

Sample Preparation – Bitumen Samples:

3. Heavy bitumen-type materials must be rendered less viscous so they can be sampled. Loosen the cap of the sample container. Place the sample container in hot water (70 to 90°C) and allow the sample to warm until the sample is fluid enough to be stirred easily with a rod. Stir thoroughly to distribute any solids present.
4. On the top loading balance, weigh to the nearest 0.01 g the still pot containing a magnetic stirring bar and fitted with a rubber stopper. Transfer approximately 100 g of the sample to the still pot. Stopper and re-weigh. Take a small portion of the sample remaining in the sample container and determine its density at 20°C using Method 3.4.

Preparation of Distillation Apparatus:

5. Half-fill the dry ice traps (see Figure 3) with isopropyl alcohol. Carefully add dry ice to the liquid in each vessel, a few pieces at a time at first to prevent the mixture from bubbling over, and then more liberally as the mixture cools. Ultimately each vessel should be filled to within 20 to 30 mm of the top. Since it will take some time to cool these vessels, it is advantageous to begin this step as soon as possible. As the run proceeds, dry ice will sublime and more should be added as replacement.
6. Label and weigh several fraction receivers and corresponding glass stoppers to the nearest 0.001 g.
7. Apply Apiezon T grease sparingly to all ground glass joints and the O-ring at the bottom of the distillation column (see Figure 2). Connect the still pot, fraction cutter, and receivers to the distillation assembly. Rotate glassware about the joints to ensure a good seal. Position the receivers to ensure their graduations are visible to the operator. Use small springs to formally attach the still pot to the column and the receivers to the fraction cutter. Insert the thermocouple into the still pot well and ensure that the thermocouple in the still head is secure. Turn on the water to the condenser.

Atmospheric Distillation:

For samples containing naphtha, IBP–195°C AET, an atmospheric distillation is performed. For samples such as bitumen, containing little or no naphtha, proceed to the vacuum distillation in step 17.

8. Set the reflux timer to provide a reflux ratio of 20:1 by setting the closed period for the reflux valve to 20 seconds and the open period to one second. Depending on the sample type, the reflux ratio may have to be adjusted. If the vapour temperature drops after a portion of distillate has been removed or if the condensation rate decreases, then the reflux ratio must be increased. Conversely, if the rate of condensation is very fast then the reflux ratio should be decreased.
9. Ensure that all stopcocks associated with the vacuum system are positioned as indicated in Figure 3. It is imperative that stopcocks D and

I be open to the atmosphere. Attempting to do a distillation in a closed system will result in a pressure increase inside the still and possible explosion. To prevent vapours entering the McLeod gauge, ensure that stopcock H is closed.

10. Raise the heating mantle to surround the bottom half of the still pot.

    Switch on the digital temperature monitor and magnetic stirrer. Set the variable transformer supply to the bottom heating mantle to 70 V and switch it on to initiate the heating. Activate the spinning band when the vapour temperature starts to rise, indicating sufficient liquid in the column to lubricate the band. Caution should be exercised during the beginning of the distillation as any water present in the sample may cause it to bump. Until this possibility is past (e.g., vapour temperature greater than 100°C), monitor the still pot closely and lower the heating mantle if bumping occurs. When there is no further potential for bumping, place the top heating mantle over the still pot.

Naphtha Fraction:

11. Obtain the atmospheric pressure reading in the laboratory from a barometer. Obtain the initial boiling point (IBP) of the sample by observing, through the reflux window, the drop point at the bottom of the condenser. The IBP is the vapour temperature at which the first drop falls. A second drop should immediately begin to form. Record the IBP as displayed on the digital temperature monitor.
12. When a condensation rate of about 2 drops/s has been established, switch on the reflux timer and immediately record the vapour temperature corresponding to a volume of 0 mL. Activating the reflux timer will cause one part of condensate to be diverted to the fraction cutter and receiver and 20 parts to return to the column. If the rate falls below 2 drops/s, the reflux timer should be shut down until this equilibrium position is again achieved. It may be necessary to increase the time that the reflux valve is closed. It is important that the condensate drops into the centre of the bend of the fraction cutter and into the centre of the graduated receiver. Adjust glassware as necessary.
13. If the sample is heated too quickly at atmospheric pressure or particularly at the lower pressure used in this distillation, excess liquid can be forced up the still into the condenser. This is termed flooding. The first indication of flooding is a flickering at the top of the column observed through the reflux window. If this occurs, switch off the reflux timer, lower the heating mantle, and turn down the variable transformer for the heating mantle slightly. When the flooding has subsided, raise the heating mantle and continue the distillation. Turn on the reflux timer when a condensation rate of 2 drops/s is achieved.
14. Record the vapour temperature for every millilitre condensate collected. Record the pot temperature at 5 mL intervals.

    It is not uncommon that a minor amount of residual water in the sample charge will distill with the naphtha and settle in the receiver. If the estimated amount of water collected exceeds 0.1 mL, record the volume and apply necessary corrections for calculating weight % distillate yields (see Calculations).
15. Continue the distillation until the vapour temperature corresponds to 195°C AET. Consult table below. Should the receiver fill to the 25 mL mark before reaching this temperature, rotate the fraction cutter to present a new receiver for incoming distillate.

Pressure		Vapour temp.
kPa	mm Hg	°C
88.1 to 90.5	661 to 679	190
90.5 to 92.9	679 to 697	191
92.9 to 95.3	697 to 715	192
95.3 to 97.7	715 to 733	193

16. Switch off the reflux timer, variable transformer for the bottom heating mantle, and magnetic stirrer in that order and immediately lower the heating mantle. Allow the fraction cutter to drain and rotate to position a new receiver. Remove and stopper the filled receiver(s) and re-weigh to the nearest 0.001 g. Replace with clean, weighed receiver(s).

Vacuum Distillation:

17. The distillation assembly is equipped with two vacuum pumps; a primary pump to evacuate the still and a secondary pump for operating the McLeod gauge. Before starting evacuation procedures, ensure that stopcock B is open to the atmosphere, that stopcock C is open between the gauge and mercury reservoir (closed to mercury trap) as indicated in Figure 4 (a). Open stopcock H and close stopcocks D and I (Figure 3). Turn on the secondary vacuum pump, and after it has started to draw a vacuum, activate the primary vacuum pump. Adjust needle valve A (Figure 1) on the bleed line until a pressure of 2.67±0.07 kPa (20.0±0.5 mm Hg) is achieved. Referring to Figure 4 (b), obtain a pressure reading in the McLeod gauge as follows:

    a. Turn stopcock C slowly to connect the mercury reservoir to the mercury trap.

    b. When the mercury rises to the first zero marking on the scale, close stopcock C to all lines.

    c. Read pressure as indicated on right hand scale.

    Evacuate the gauge as instructed below and illustrated in Figure 4 (d):

    a. Turn stopcock B to connect the secondary vacuum line and the mercury trap.

    b. When a vacuum is achieved, turn stopcock C to connect the mercury reservoir to the trap.

    c. When all mercury returns to the reservoir, rotate stopcock C to connect the gauge and reservoir, and stopcock B to connect the atmosphere and mercury trap (as illustrated in Figure 4 (a)).

    If the observed pressure reading deviates from 2.67±0.07 kPa (20.0±0.5 mm Hg), adjust the bleed valve. Wait for equilibrium and repeat the pressure measurement and gauge evacuation procedures.

18. Raise the heating mantle to surround the bottom half of the still pot. Switch on the temperature monitor and the magnetic stirrer. Bitumen samples may be too viscous to stir until the pot temperature reaches approximately 100°C.

    Set the variable transformer for the bottom heating mantle to 70V and switch it on to initiate the heating. Activate the spinning band when the vapour temperature starts to rise, indicating sufficient liquid in the column to lubricate the band. Again, caution should be exercised during the beginning of the distillation as any water present in the sample may cause it to bump. Until this possibility is past, monitor the

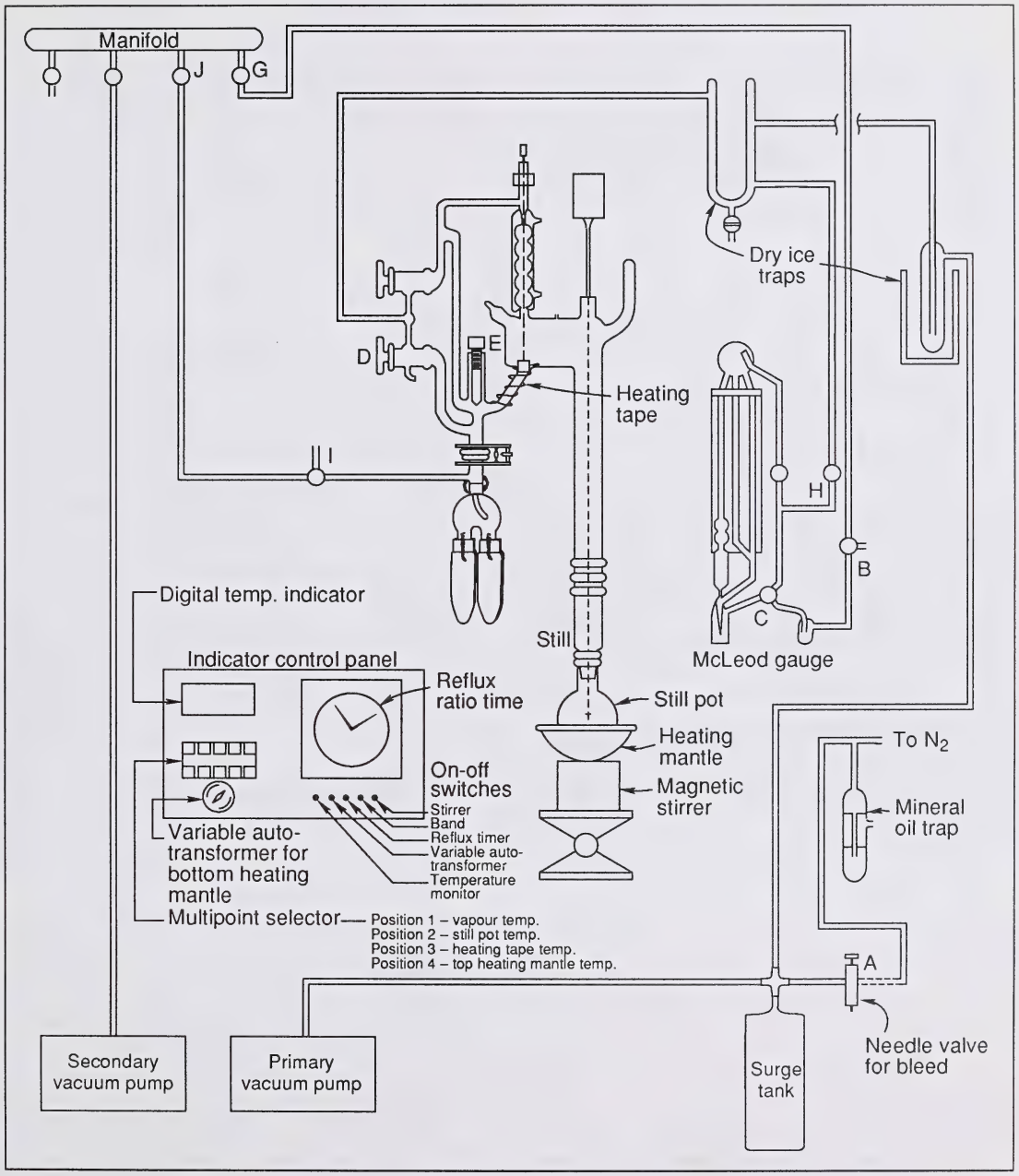

Figure 1. Complete distillation assembly.

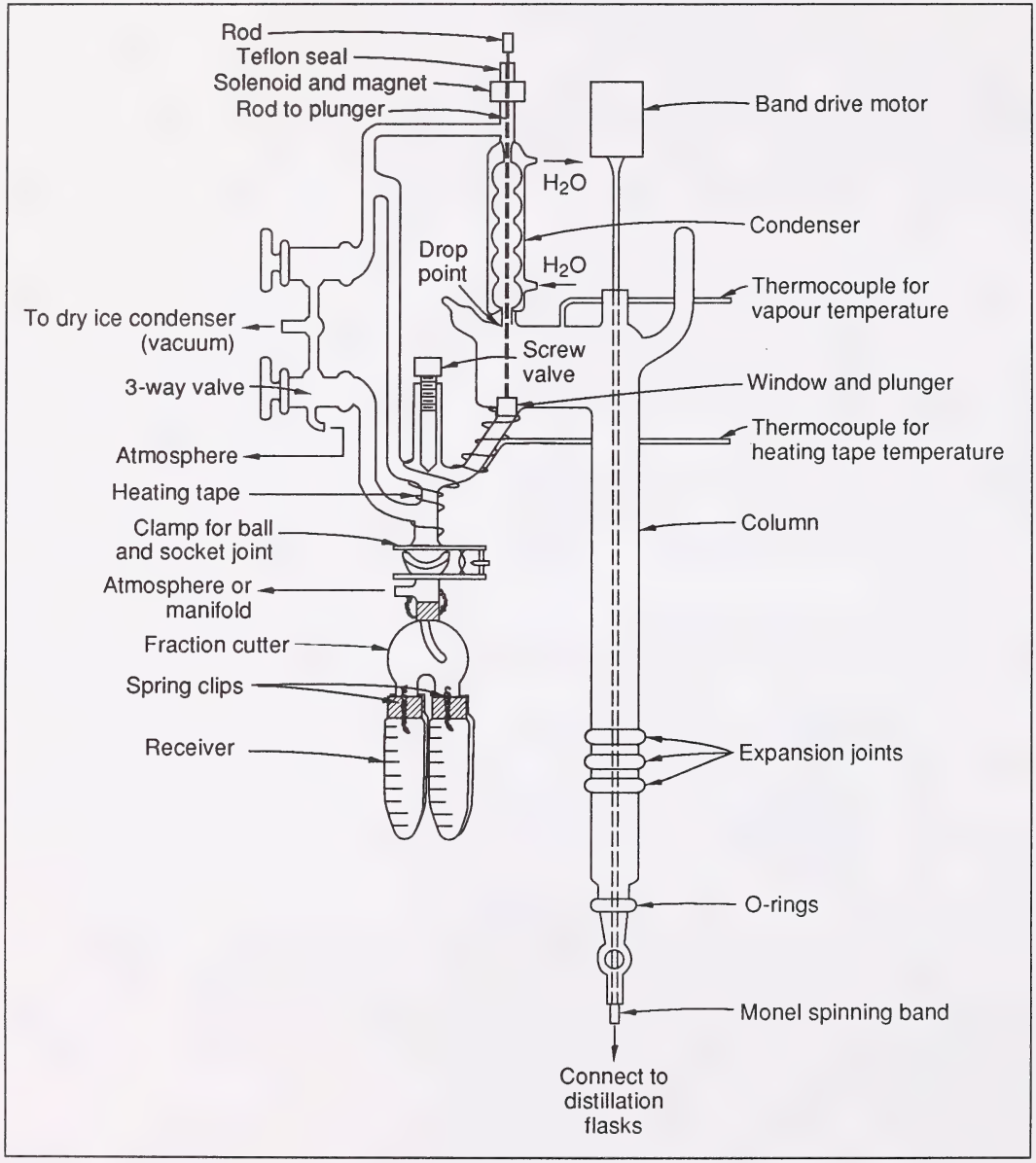

Figure 2. Distillation apparatus.

still pot closely and lower the heating mantle if bumping occurs. When there is no further potential for bumping, place the top heating mantle over the still pot.

Light Gas Oil Fraction:

19. For bitumen samples or samples containing no naphtha fraction, obtain the initial boiling point (IBP) of the sample by observing, through the reflux window, the dropping point at the bottom of the condenser. The IBP is the vapour temperature at which the first drop falls. A second drop should immediately begin to form. Record the IBP as displayed on the digital temperature monitor.
20. When the condensation rate of about 2 drops/s has been established, switch on the reflux timer, set at a reflux ratio of 3:1 (see step 8) and immediately record the vapour temperature corresponding to a volume of 0 mL. Activating the reflux timer will cause one part of condensate to be diverted to the fraction cutter and receiver and three parts to return to the column. If the rate falls below 2 drops/s, the reflux timer should be shut down until this equilibrium position is again achieved. The reflux ratio may need to be adjusted. It is important that the condensate drops into the centre of the bend of the fraction cutter and into the centre of the graduated receiver. Adjust glassware as necessary.

    If the sample is heated too quickly at the low pressures used in this distillation, flooding may occur. The first indication of flooding is a flickering at the top of the column observed through the reflux window. If this occurs, switch off the reflux timer, lower the heating mantle, and turn down the variable transformer for the bottom heating mantle slightly. When the flooding has subsided, raise the mantle and continue the distillation. Turn on the reflux timer when a condensation rate of 2 drops/s is achieved.
21. Record the vapour temperature for every millilitre of condensate collected. Record pot temperature at 5 mL intervals. Monitor and record system pressure several times during the distillation.
22. Some bitumen samples may contain a small amount of naphtha, i.e., components with bp <85°C at pressures of 2.67±0.07 kPa (20.0±0.5 mm Hg). If any naphtha has been collected the receiver should be rotated to present a new one when the vapour temperature reaches 85°C.
23. Continue to collect the LGO distillate until the vapour temperature corresponds to 343°C AET at the pressure registered. Consult the table below which gives combinations of pressure and vapour temperature that yield an AET of 343°C when a K factor of 11.1 is used.

Pressure		Vapour temp.
kPa	mm Hg	°C
2.60 to 2.64	19.5 to 19.8	209
2.65 to 2.73	19.9 to 20.5	210

Heavy Gas Oil Fraction:

24. Present a new receiver and continue the distillation at 2.67±0.07 kPa (20.0±0.5 mm Hg). If necessary, turn up the variable transformer for the bottom heating mantle until the vapour temperature is 270–280°C for

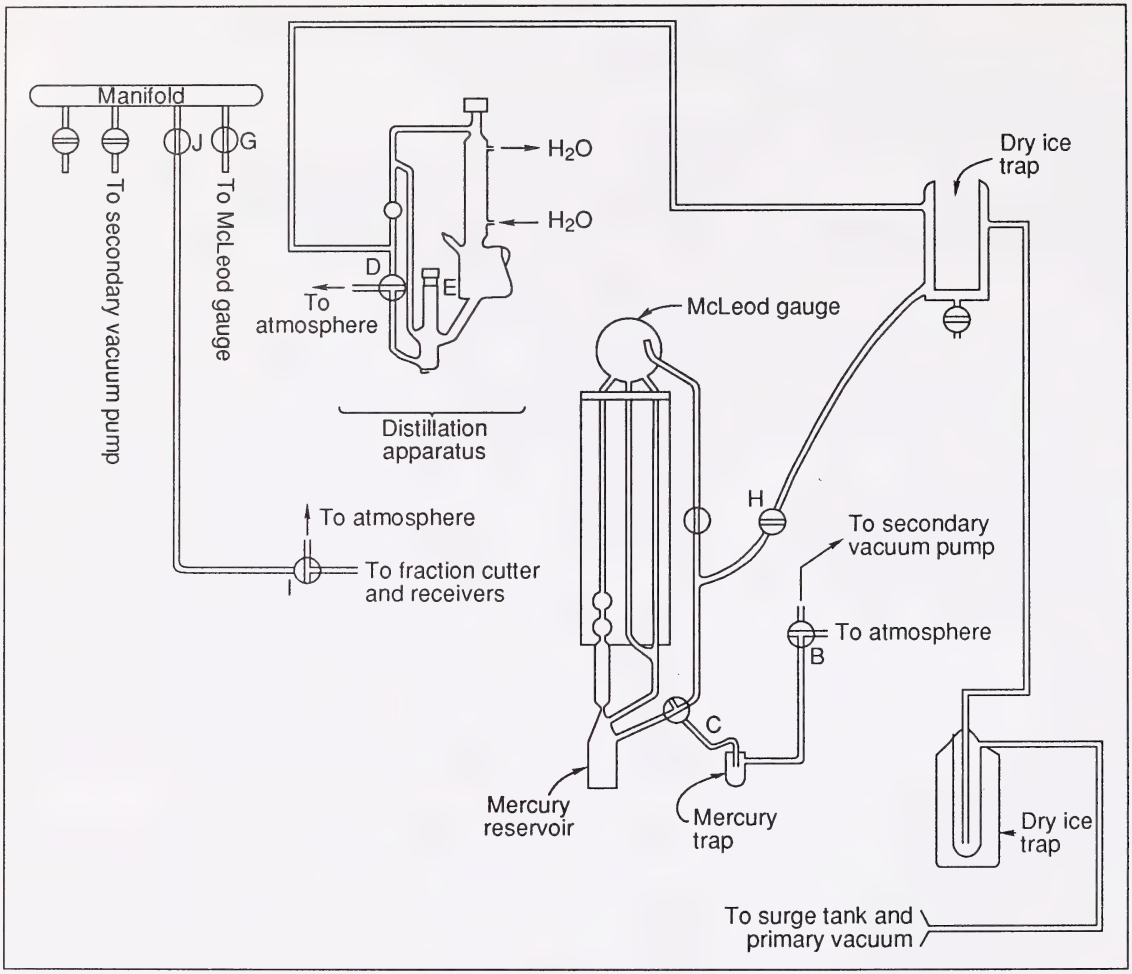

Figure 3. System layout for vacuum distilaltion.

liquid hydrocarbon samples or 230–250°C (or 300–340°C pot temperature) for bitumen samples. As necessary, turn on and adjust the temperature of the top heating mantle but ensure that its temperature is less than the vapour temperature. At the specified temperature turn off the reflux timer, spinning band, and magnetic stirrer in the sequence specified and immediately lower the heating mantle. The variable transformer for the heating mantle is not turned off.

i. Close stopcock D to all lines and screw plunger E tightly closed (see Figure 3).

ii. Close stopcock J and cautiously open stopcock I to the atmosphere.

iii. Remove LGO receiver(s), stopper and replace with new one(s). Do not remove the HGO receiver.

iv. Return stopcock I to its original position (closed to atmosphere, open to system) and slowly open stopcock J to evacuate the system using the secondary vacuum pump. After one to two minutes, close stopcock J and turn stopcock D very slowly to its original position. Open screw plunger E.

Weigh the stoppered LGO receiver(s) to the nearest 0.001 g.

25. Distillation of the remainder of the HGO fraction in the sample is conducted at approximately 80 Pa (0.6 mm Hg) pressure. Cool until the pot temperature and vapour temperature are less than 150°C before applying this vacuum. Adjust needle valve A (Figure 1) on the bleed line until the McLeod gauge indicates a pressure of 80±7 Pa (0.60±0.05 mm Hg). Note that the mercury level in the McLeod gauge is initially adjusted to the second zero mark with pressure readings taken from the centre scale (see Figure 4). Pressures below 67 Pa (0.5 mm Hg) cannot be used because of the pressure drop between the still head and McLeod gauge.

26. Raise the heating mantle to surround the lower half of the still pot. Switch on the magnetic stirrer. Turn on and adjust the variable transformer controlling the heating tape on the column delivery arm to provide a temperature of approximately 100°C. Turn down the variable transformer for the bottom heating mantle to 70 V when the vapour temperature begins to rise. Activate the spinning band when sufficiently lubricated and turn on the reflux timer when a condensation rate of 2 drops/s has been established. Use Table 1 as a guide for switching on the reflux timer.

    If the HGO part of the distillation is rushed, a smooth distillation curve will not be obtained.

    Monitor the temperature within the still pot very closely. Normally the pot temperature rises at a rate of 3±1°C/mL of condensate collected. After a few millilitres of distillate have been collected, both the rate of temperature rise and the condensation rate will subside. At this point advance the variable transformer setting for the bottom heating mantle to 75 V (and later to 80 V, if necessary) to maintain the required temperature control. Record the vapour temperature and pot temperature at every millilitre of condensate collected. Monitor and record system pressure several times during the distillation of the HGO fraction.

27. Continue the distillation until the observed vapour temperature corresponds to 524°C AET at the pressure registered. Consult the table below which gives various combinations of pressure and vapour temperature that yield an AET of 524°C when a K factor of 11.1 is used.

Pressure		Vapour temp.
kPa	mm Hg	°C
73 to 76	0.55 to 0.57	279
77 to 80	0.58 to 0.60	280
81 to 83	0.61 to 0.62	281
84 to 87	0.63 to 0.65	282

Record the still pot temperature when the 524°C AET is reached. For samples containing little residue, it may not be possible to reach a 524°C AET end point. Discontinue the distillation when there is insufficient material in the still pot to allow the distillation to proceed. If the pot

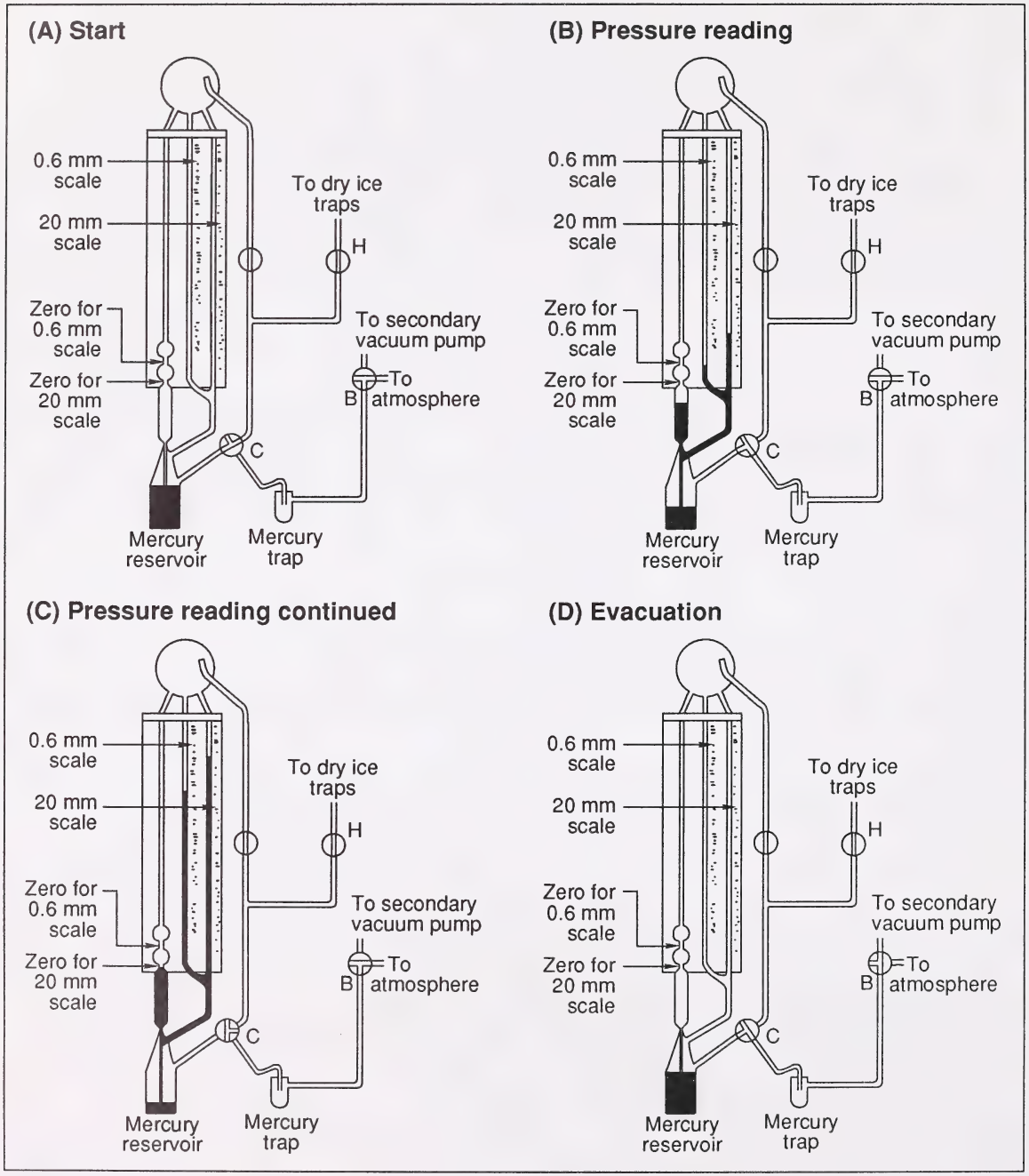

Figure 4. McLeod gauge operation.

Table 1. Guide for switching on the reflux timer

Vapour temperature at 2.67 kPa (20.0 mm Hg) pressure	AET	Vapour temperature at 80 Pa (0.60 mm Hg) pressure
°C	°C	°C
Liquid hydrocarbons		
270	412	189
271	413	190
272	414	191
273	415	191
274	416	192
275	417	193
276	419	195
277	420	195
278	421	196
279	422	197
280	423	198
Bitumen		
230	366	153
231	367	154
232	368	154
233	370	156
234	371	157
235	372	157
236	373	158
237	374	159
238	375	160
239	376	161
240	378	162
241	379	163
242	380	164
243	381	164
244	382	165
245	383	166
246	384	167
247	386	168
248	387	169
249	388	170
250	389	171

temperature reaches 360°C for bitumen samples, record the vapour temperature at that point and discontinue the distillation. Switch off the reflux timer, power to the bottom heating mantle, spinning band, and magnetic stirrer in that order and immediately lower the heating mantle. Allow the fraction cutter to drain and then position a new receiver. Remove, stopper, and weigh the HGO receiver(s).

28. For bitumen samples begin to flow nitrogen in the nitrogen tubing. Connect it to the "T" on the surge tank. Switch off the vacuum pumps one at a time. Slowly open the bleed on the surge tank while observing the mineral oil trap. If the mineral oil begins to rise out of the trap the bleed is being opened too quickly and should be adjusted. When the system is at room pressure, disconnect the nitrogen tubing from the T

and turn off the nitrogen. Remove the still pot from the column. Stopper lightly and weigh to the nearest 0.01 g when cooled.

For liquid hydrocarbon samples, remove the still pot.

Hold-up and Column Cleaning:

29. Fill a 50-mL still pot approximately two-thirds full with toluene. Add a small magnetic stirring bar and attach the flask to the distillation column. Ensuring that stopcock D is open to the atmosphere, raise the heating mantle, set the variable transformer to 60 V, and begin heating. Toluene condensate descending down the column will dissolve residual hydrocarbons contained in the system and carry them down to the flask.
30. After the toluene vapours climb at least one-third up the condenser, turn on the spinning band and reflux timer. Collect the distillate in a clean receiver. When the column is clean, switch off all equipment and lower the heating mantle. Transfer the contents of the flask and receiver to a previously weighed (0.001 g) crucible. Allow the toluene to evaporate overnight at ambient temperatures and weigh crucible to obtain the amount of hold-up.

Cleaning the Still Pot:

31. For bitumen samples, add liquid nitrogen to the residue in the still pot. When the mass is sufficiently brittle, break into small pieces with a spatula. Empty the broken material into a clean sample container if further analytical use is required. The wall of the flask can be cleaned by immediately rinsing with toluene.

CALCULATIONS:

Distillation Curve:

In order to construct a distillation curve from distillate volumes and corresponding vapour temperatures, it is necessary to convert vapour temperatures to atmospheric equivalent temperatures and volumes to volume percents. The former is accomplished using the Sydney Young equation (2) for the atmospheric distillation and the Maxwell and Bonnell equation (3,4) for distillation under reduced pressures. The Maxwell and Bonnell equations presented below have been modified to accommodate degrees Celsius inputs and corrected for the effect of hydrocarbon type (UOP Characterization Factor K).

1. Sydney Young Equation

$$AET\,(°C) = T_v + 0.00012\,(760 - P)\,(273 + T_v)$$

where: T_v = vapour temperature (°C)

$$P = \frac{\text{pressure (Pa)}}{133.3}\ \text{pressure (mm Hg)}$$

2. Maxwell and Bonnell Equation

$$AET\,(°C) = \frac{5}{9}\left(\left[\frac{748.1A}{\frac{1}{1.8T_v + 491.6} + 0.2145A - 0.0002867}\right] - 491.6\right) + \Delta T$$

where: A = constant related to the vapour pressure derived from data in reference 4

$$= 5/9 \log \left(\frac{760}{P} \left[-2.5 \ (K \quad 12.0) \right] \right)$$

ΔT = correction for the K-factor

$$= \frac{7.6723 - \log P}{3410.77}$$

T_v = vapour temperature (°C)

$$P = \frac{\text{pressure (Pa)}}{133.3} \quad \text{pressure (mm Hg).}$$

3. Volume % Distillate:

Volume % distillate =

$$\frac{\text{Cumulative volume of distillate (mL)}}{\text{Sample weight (g)}} \times \text{Sample density (kg/L)} \times 100$$

Report temperature to the nearest whole number and volume % distillates to the nearest 0.1%. Plot volume % distillate versus AET (°C) on rectangular coordinate paper to provide a distillation curve characteristic of the original sample.

Distillate Yields:

1. Naphtha fraction (IBP–195°C AET)

$$\text{Weight \%} = \frac{\text{Weight naphtha fraction}}{\text{Sample weight}} \times 100 \qquad (1)$$

If a significant volume of residual water distilled over with the naphtha fraction (> 0.1 mL), correct sample weights and weight of naphtha collected by subtracting from these the observed volume of water (1 mL H_2O = 1 g).

2. Light gas oil fraction (195–343°C AET)

$$\text{Weight \%} = \frac{\text{Weight LGO fraction}}{\text{Sample weight}} \times 100 \qquad (2)$$

3. Heavy gas oil fraction (343–524°C AET)

$$\text{Weight \%} = \frac{\text{Weight HGO fraction}}{\text{Sample weight}} \times 100 \qquad (3)$$

4. Residue (>524°C AET)

$$\text{Weight \%} = \frac{\text{Weight residue}}{\text{Sample weight}} \times 100 \quad (4)$$

5. Hold-up

$$\text{Weight \%} = \frac{\text{Weight hold-up}}{\text{Sample weight}} \times 100 \quad (5)$$

6. Total recovery

Weight % = (1) + (2) + (3) + (4)

PRECISION: Precision data reflecting the repeatability of weight% distillate fraction determinations for a typical bitumen and virgin gas oil are indicated below. Results are based on four or more complete distillations performed by a single operator on charges obtained from homogeneous stock.

	Mean value (wt%)	Standard deviation (wt%)	Relative standard deviation
Bitumen			
LGO	12.50	±0.16	1.25%
HGO	27.24	±0.53	1.96%
Residue	58.23	±0.29	0.50%
Recovery	99.26	±0.10	0.10%
Virgin Gas Oil			
Naphtha	2.18	±0.12	5.32%
LGO	22.84	±0.44	1.91%
HGO	67.17	±0.27	0.40%
Residue	5.59	±0.10	1.74%
Recovery	99.58	±0.13	0.13%

For the bitumen sample the distillations were discontinued when cracking became evident.

COMMENTS: A 67 Pa (0.5 mm Hg) lower limit to the pressure is characteristic of the particular arrangement employed by Syncrude Research.

REFERENCES:

1. Yost, R.W., "Distillation Primer, Survey of Distillation Systems," American Laboratory, January 1974, p. 63.
2. ASTM Method D 86, "Distillation of Petroleum Products."
3. Maxwell, J.B. and Bonnell, L.S., "Derivation and Precision of a New Vapour Pressure Correlation for Petroleum Hydrocarbons," Ind. Eng. Chem., 49, 1187 (1957).
4. Maxwell, J.B. and Bonnell, L.S., "Vapor Pressure Charts for Petroleum Hydrocarbon," Esso Research and Engineering Co., Linden, NJ, April 1955. Available on request.
5. UOP Method 375, "Calculation of UOP Characterization Factor and Estimation of Molecular Weight of Petroleum Oils."

D1160 Automatic Distillation of Bituminous Material

INTRODUCTION: This distillation method provides for the determination of empirical distillation characteristics of petroleum products and fractions which may decompose when distilled at atmospheric pressure. The distillate fractions may be collected for additional analysis. The apparatus currently used is capable of generating only two fractions, namely a distillate fraction and a residue fraction, from an initial sample charge.

SCOPE: This method describes the determination of the boiling temperature ranges of bitumen-type samples which can be vapourized at a maximum liquid temperature of 400°C at pressures ranging from 1 to 10 mm Hg.

SUMMARY: The sample is distilled at reduced pressure utilizing conditions that provide approximately one theoretical plate fractionation. Data from the simultaneous reading of distillate volume and vapour temperature is converted to atmospheric equivalent temperature, thereby providing a distillation curve typical of the sample.

SAFETY CONSIDERATIONS:

1. Toluene: highly flammable, flashpoint 4°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis .
2. Liquid Nitrogen: freezes skin. Wear protective gloves.
3. Glassware under reduced pressure is capable of implosion. Keep safety door closed while apparatus is under vacuum.

WASTE DISPOSAL: Dispose of waste or excess sample materials in appropriate hydrocarbon tank marked for waste only.

APPARATUS, REAGENTS, AND MATERIALS:

1. Herzog MC-630 Automatic Vacuum Distillation Apparatus.
2. Toluene, reagent grade.
3. Liquid Nitrogen.

SAMPLE CONSIDERATIONS:

Amount Required:	250 mL
Properties:	Samples must vaporize below the maximum liquid temperature of 400°C.
Interferences:	Sample containing large quantities of dissolved gases bump easily.
	Samples containing water must be dried prior to analysis.

PROCEDURE: Calibration:

1. The calibration of the receiver should be checked every three or four months, or whenever a new or different receiver is used.
2. Place a clean, dry receiver into position with the mark on the receiver facing forward.

3. Select the diagnostic program from the program menu.
4. Locate the "VOL-ADJUST" on the screen and, using the light pen, push once to set to zero. The screen should say "ZERO" on the "VOL-ADJUST" line.
5. The meniscus follower will go to the base of the receiver and the display for "VOLUME" on the screen will read:

   either < .0 mL

   or > .0 mL

   or * .0 mL

   the proper display is * .0 mL.
6. If the asterisk is not present, adjust the zero ajustment on the front lower left of the control unit until the asterisk appears. Turn counter-clockwise to increase, clockwise to decrease.
7. Change the "VOL-ADJUST" to display "SPAN." Then remove the receiver.

   Note: The "VOL-ADJUST" must be switched to "SPAN" before removing the empty (zero) receiver so that the MC630 can remember the zero.
8. Pipet, using a 200-mL pipette, exactly 200 mL of toluene into the receiver and re-position the receiver into the unit.
9. The meniscus follower will track up to the meniscus of the toluene and the "VOLUME" on the screen will read:

   either < 200

   or > 200

   or * 200

   the proper display is * 200
10. If the asterisk is not present, adjust the span adjustment on the front lower left of the control until the asterisk appears. Turn counter-clockwise to increase, clockwise to decrease.
11. Use the light pen to press once on the "VOL-ADJUST" line, there will be no display on the "VOL-ADJUST" line. Remove the receiver, clean and dry.
12. Repeat steps 1–10 until the "VOLUME" displays the proper values without having made any further adjustments to either the zero or span.

Calibrations of the Pressure System:

13. The pressure systems need only to be calibrated when a new transducer is used. It should be noted that the transducers require a warm-up period of at least one hour.
14. Remove the covers from the left front control panel.
15. Assemble the distillation apparatus using an empty flask and receiver.
16. The following procedure is set out using a 10 mm transducer. The procedure is similar for the 1 mm transducers.
17. Set point pressure:
    a. Use the parameter screen, input an operating pressure of 1 mm Hg.
    b. Start distillation.

c. Read the display on the pressure controller monitor at the top of the panel.

d. Adjust the zero (P4) such that the pressure controller reads 1.000.

e. Stop the distillation and input 10 mm Hg as the operating pressure. Re-start the distillation.

f. Adjust the span (P3) to read 10.000 on the pressure controller.

g. Repeat until both set points read correctly without having made any further adjustments.

Note: the zero and span are located on the interface board, third from the bottom. The board (606-71 PCB) is labelled on the right side of the rack.

P4 zero	P3 span	P2 zero	P1 span	
set point			process pressure	606-71PCB

18. Process pressure:

a. Use either the graphic or the diagnostic screen.

b. At the setpoint of 1 mm Hg, adjust the zero (P2) such that the pressure on the graphic screen or under actual pressure on the diagnostic screen reads the same as the display on the pressure controller monitor.

c. At the setpoint of 10 mm Hg, adjust the span (P1) until the pressure reads the same as the display on the monitor.

d. Repeat until the pressures at zero and span read correctly without further adjustment.

Note: when calibrating the 1 mm Hg transducer, the pressure controller monitor will display 1.000 for 0.1 mm Hg and will display 10.000 for 1.0 mm Hg.

Distillation Procedure:

1. Pre-heat the sample to approximately 50°C by placing the sample, in a closed jar, in an oven set at 70°C for 30 minutes. To obtain reproducible results, samples should not be left in the oven for longer than 30 minutes. The volume of the sample is calculated using the density at the receiver temperature (60°C); therefore, the sample weight should be recorded at 60°C. Pre-heating the sample also reduces the viscosity and aids in the transfer of the sample into the distillation flask.

2. Selection of distillation parameters:

Distillation programs containing typically-used parameters can be stored and retrieved as necessary. Using the light pen, select a distillation program from the sample type storage screen. To change any distillation parameter, place the light pen on the parameter and enter the new values from the numbers appearing on the bottom of the screen.

3. Sample description and sample number:

A screen with a keyboard will appear. Clear the entry and type in a new sample description. Press ENTER. This will enter the new description

and return the user to the distillation program screen. Repeat to change the sample number.

4. Sample volume:

   The volume is calculated from the density and sample weight entered into the program. No user entry is required.

5. Receiver temperature:

   The temperature of the receiver is normally set at 60°C to keep the distillate fluid enough to flow to the bottom of the receiver.

6. Density:

   The density of the sample at 60°C, the receiver temperature, is entered into the program. This value is entered as kg/m^3. For example, a density of 0.994 g/mL is entered as 994.

7. Mass:

   The weight of the sample is entered to the nearest 0.1 g.

8. Distillation stop at volume %:

   The value is set at the default value of 90%.

9. Initial heat rate:

   This value is normally set at a rate of 4°C per minute to enable the distillation to proceed at the ASTM rate of about 4 mL/min.

10. Operating pressure:

    The distillation is normally run at 1 mm Hg.

11. Distillation rate:

    This is normally set at 4 mL/min.

12. Condenser temperature:

    The maximum temperature of the condenser is set at 90°C to enable the distillate to flow freely to the receiver, thereby avoiding a build-up of material in the condenser.

13. Delta T vapour:

    The delta T vapour is set at 30°C. This maintains a 30° differential between the vapour temperature and the condenser temperature, allowing the lower boiling point components to condense, until the temperature reaches the maximum condenser temperature of 90°C.

14. Temperature/volume points:

    This screen allows selection of the various distillation points of interest to be shown on the distillation report. It also allows the distillation to be stopped at a pre-selected temperature or volume. Temperatures of interest can be chosen in the first column, typically used are 343 and 524°C. The second column allows the user to select whether these are to be the actual temperature (ACT), the liquid temperature, or, more typically, atmospheric equivalent temperature (A.E.). Various volumes and their corresponding temperatures can be shown on the report from selections in column three. The fourth column gives the user the opportunity to end the distillation at any of the proceeding points. Table 1 shows typically chosen temperature and volume points.

15. Weigh 200 g (to the nearest 0.1 g) into a pre-weighed distillation flask and enter this weight into the distillation program. See above.

16. Lightly grease the still connections and position the distillation flask and the receiver into the unit. The drip catcher is inserted into the neck of

Table 1.

Temperature °C	Liquid A.E./ACT	Volume Vol%	End Yes/No
343	A.E.		No
500	A.E.		No
524	A.E.		No
550	A.E.		No
	A.E.	10	No
	A.E.	20	No
	A.E.	30	No
	A.E.	40	No

the receiver such that it rests on the two glass constrictions. The receiver is positioned so that the drip catcher and the mark on the receiver faces toward the front. The holding clamps are tightened to finger-tight only.

17. De-gassing the sample:

    The five de-gassing cycles incorporated in the distillation program are insufficient for removing all the dissolved gases in a typical bitumen sample. Therefore the de-gassing is done manually using the diagnostic program. The procedure is as follows:

    a. Select the diagnostic program from the program menu.

    b. Turn the heater relay to the "ON" position.

    c. Using the light pen, press distillation heater three times until the voltage shown ramps upward. Continue ramping the heater until the liquid temperature reaches approximately 70°C. To avoid "bumping" of the sample, the liquid temperature should not be allowed to increase too rapidly.

    d. Close SV trap drain outlet.

    e. Reduce the pressure slowly by turning the vacuum pump on and off rapidly. Avoid excessive frothing of the sample.

    f. When the pressure reaches 1 mm Hg, leave the vacuum pump on for two to three minutes until the frothing is relatively controlled.

    g. End diagnostic program.

18. Start the distillation program. During the distillation, any of the screens may be viewed, however, no additional information can be entered. The distillation can be stopped at any time by pressing "STOP" on the screen.

    The distillation will automatically end when the pot temperature reaches 400°C or the transducer senses cracking. The distillation will also stop at any pre-selected temperature or volume point. The operator cannot gain access to the distillation apparatus until the pot temperature has been cooled to 110°C and the pressure has been increased to atmospheric. The tone is stopped by pressing "ACK" on the screen.

19. Clean-up:

    a. Remove the temperature probe while the liquid temperature is between 90 to 110°C to avoid breakage of the glass tip.

    b. Remove the distillation flask and receiver. Replace with a clean flask containing approximately 100 mL of toluene and a clean receiver.

c. Return to the menu screen and select the "START CLEANING CYCLE."

d. The residue formed in the distillation flask can be removed by using liquid nitrogen. When the residue is sufficiently brittle, use a spatula to break it into small pieces. Subsample the residue and distillation as necessary for further analysis. Clean the flask and receiver with toluene, rinse with acetone, and air dry.

Note: Do not use acetone in the distillation apparatus.

Obtaining Distillation Cuts:

20. The procedure for obtaining distillation cuts is essentially the same as doing separate distillations.

a. To make the first cut in the distillation, follow the same procedure as outlined above; enter the selected end point into the temperature/volume point screen. For example, to obtain the light gas oil cut, enter "343" into the temperature column, "A.E." (atmospheric equivalent) into the second column, and "YES" in the end distillation column as shown in Table 2.

Table 2.

Temperature °C	Liquid A.E./ACT	Volume Vol%	End Yes/No
343	A.E.	*7.7*	Yes
500	A.E.		No
524	A.E.		No
550	A.E.		No
	A.E.	10	No
	A.E.	20	No
	A.E.	30	No
	A.E.	40	No

b. At the end of the distillation, when the pot temperature has been cooled to 110°C and the pressure returned to atmospheric, remove the receiver and subsample the cut for further analysis. Clean and dry the receiver.

Note: The same calibrated receiver must be used for all the distillation cuts.

c. Clear the previous entry from the temperature/volume point screen and enter the next distillation end point.

d. Re-enter the sample weight into the distillation program.

e. Start the distillation program. At this point, the manual de-gassing step is no longer necessary.

f. Continue these steps (a–e) until all the required cuts have been collected.

g. Clean the distillation apparatus as outlined above.

Routine Maintenance:

1. Vacuum pump:

a. Check the level of the oil daily.

b. The oil should be changed when the oil appears darkened, has a distinctly unusual odour, or metallic impurities are felt when rubbing a drop of oil between thumb and forefinger.

2. Distillation Apparatus:
   a. Check the alignment of the still periodically.
   b. Periodically remove the transducer and clean the column condenser with toluene. Do not use acetone. Re-grease and re-assemble.
3. Video Screen:

   Clean the screen periodically with glass cleaner (Windex) to remove dust and oil film.

CALCULATIONS: All of the calculations are carried out automatically by the microprocessor. It is possible to alter the Watson K factor used in the equations which calculate the atmospheric equivalent temperature.

REPORT FORM: A complete distillation report and curve are printed at the end of the distillation. An example is shown in Figure 1. The standard D1160 Data Sheet is given in Figure 2.

PRECISION: The precision of the distillation has been evaluated by replicate distillations of a bitumen sample. The results are given in Table 3.

Table 3. Automated distillation of bitumen

Volume % off	Average atmospheric equivalent temperature	Standard deviation (ls, n = 7)
	°C	°C
IBP	248.5	20.5
5	321.6	2.9
10	348.8	3.4
15	373.3	1.9
20	399.3	1.8
25	424.9	1.5
30	449.5	1.3
35	475.0	1.8
40	501.1	1.6
45	526.9	1.2
Cracking	532.3	1.2

TIME CONSIDERATIONS:

Time Per Analysis:	2 h
Technician Contact Time:	30 min
Samples Per Day:	3
Calibration Time:	1 d (only periodically required)

REFERENCE: ASTM Method D1160, "Distillation of Petroleum at Reduced Pressures."

HERZOG MC 630 ASTM D-1160

Sample description		: ZETON FEED				
Sample number		: 0913 6/FEB/91				
Dist. program		: 8				
Dist. stop at	vol%	: 90	Sample volume	mL	: 200.0	
Initial heat rate	K/min	: 4	Density (60°C)	kg/m^3	: 1000	
Operating pressure	mmHg	: 1	Mass	g	: 200.0	
Dist. rate	mL/min	: 4	C-factor		: 12	
			Delta T vapour			
Condenser temp.	°C	: 90	– Condenser	°C	: 30	
Receiver temp.	°C	: 60	– Receiver	°C	: 60	

Time min °C	Volume vol% A.E/ACT	Act-Temp °C vol%	Press mmHg Yes/No	A.E-Temp °C	Liquid Temp °C	Temp	Liquid/	Volume	End
26.6	IBP	96.1	1.06	275.9	160.3	343	A.E.	* 6.6*	No
mL/min						400	A.E.	* 17.9*	No
2.0	5	139.6	1.07	332.2	189.6	433	A.E.	* 25.0*	No
2.9	10	163.5	1.08	362.3	213.0	450	A.E.	* 28.5*	No
3.4	15	179.7	1.06	383.2	235.6	500	A.E.	* 38.9*	No
3.5	20	201.5	1.08	409.7	258.4	524	A.E.	* 44.1*	Yes
3.8	25	221.1	1.08	433.8	278.5	550	A.E.		No
3.7	30	240.4	1.09	457.0	299.7		A.E.		No
3.6	35	260.5	1.08	481.3	322.2		A.E.		
3.4	40	202.1	1.11	506.3	250.3	Liquid temperature static			
Dist. stop at									
	44.0	296.8	1.13	523.0	369.4				

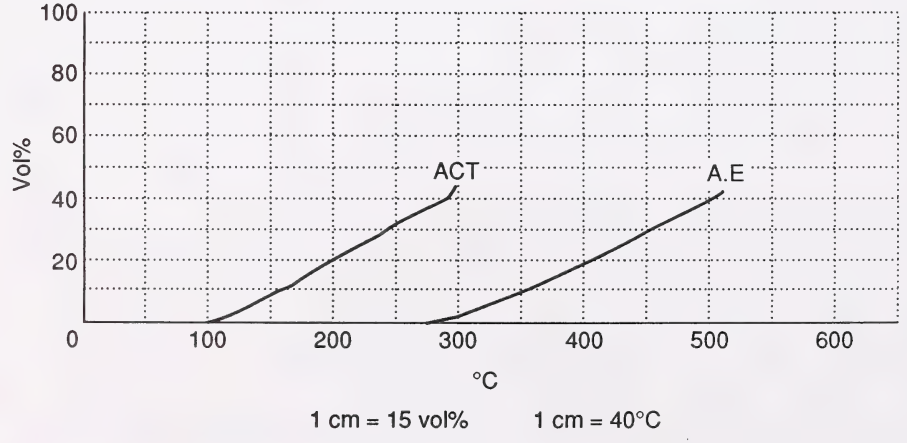

Figure 1. Sample distillation report and graph.

			Sample		Distillate				Residue				Density		
Date	Tag no.	Sample type	Wt. flask & chips	Wt. sample	Wt. rec. & dist.	Wt. rec.	Wt. dist.	Wt% dist.	Wt. rec.	Wt. flask & chips	Wt. res.	Wt% res.	25°C	15°C	60°C

Figure 2. Standard D1160 data sheet.

5

CATALYST CHARACTERIZATION

Elemental Analysis of Syncrude Process Catalysts

INTRODUCTION: Syncrude upgrading catalysts are designed to facilitate hydrotreating and cracking as well as to remove sulphur and metals found in the feedstock. As the metals and sulphur build up over a period of time on the catalyst, activity decreases. It is therefore of advantage for process optimization to monitor any catalyst removed during the operating period for the amount of metals and sulphur accumulated. This requires knowledge of the typical metallic composition of fresh, intermediate, and exhausted (spent) catalyst as well as the feedstock and products. Analysis of the fresh catalyst also serves as a quality control procedure as new lots of catalyst are purchased.

SCOPE: This method determines the amount of Ni, V, Fe, Al, Co, Si, S, and Mo in a catalyst sample (fresh or spent).

SUMMARY: A 1-g sample of catalyst is shattered, then ashed at either 400 or 538°C, determined by the catalyst type, for four hours. A 0.1000 g subsample is fused at 1000°C for 30 minutes with lithium metaborate. The melt is dissolved with 20% nitric acid, diluted with de-ionized water, and aspirated into the Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP-AES). The high-energy-RF-field induced emission of light at the atomic level, as detected by an optical spectrometer, provides an indication of the relative amounts of the various elemental species present. Concentrations are then determined with respect to a known standard previously prepared and analyzed in the same manner.

BACKGROUND: The analysis of metals in a variety of Syncrude upgrading catalyst samples can be accomplished using a number of different analytical techniques. The most commonly used techniques include Inductively Coupled Argon Plasma Atomic Emission Spectrometry (ICAP-AES), atomic absorption Spectrometry (AA), and X-ray fluorescence spectrometry (XRF). Each provides different sensitivities and requires significantly different sample preparation methodology. For the specific case of bitumen hydrotreating and hydrocracking catalyst, the ICAP-AES provides a method relatively free of matrix interferences that are problematic in other methods.

SAFETY CONSIDERATIONS:

ICAP Spectrometer:

1. Avoid direct exposure to the high intensity ultra-violet light produced by the plasma.
2. Caution is also required when dealing with the ICAP instrumentation due to the very high power present.

Nitric Acid:

1. Extremely corrosive, strong oxidizing agent.
2. Refer to Material Safety Data Sheet (MSDS).

Catalyst:

May be pyrophoric, auto-ignition may occur during drying stage. Use a nitrogen-purged drying oven, especially for spent catalyst that is not fully deactivated. Refer to Material Safety Data Sheet (MSDS).

Toluene:

1. Highly flammable, flashpoint 20°C. Harmful vapour; irritates eyes and mucous membranes, may cause dizziness, headache, nausea, and mental confusion. Liquid can be absorbed through skin. Liquid may cause dermatitis.
2. Refer to Material Safety Data Sheet (MSDS).

Muffle Furnace:

High temperatures, radiative heat, hot surfaces. Refer to owner's manual for safe operating instructions.

APPARATUS, REAGENTS, AND MATERIALS:

1. Inductively Coupled Argon Plasma Spectrometer:
   Applied Research Laboratories,
   MODEL 3580,
   Applied Research Laboratories,
   Valencia, CA., U.S.A
2. Pump:
   Gilson Minipuls Model MPl,
   Gilson Medical Electronics Inc.,
   West Beltine Highway,
   Middleton, WI., USA
3. Porcelain Crucibles
4. Volumetric Flasks: 100, 250, 500 mL Class A.
5. Nitric Acid: A.C.S.: Reagent Grade.
6. De-ionized water.
7. Toluene: A.C.S. : Spectral Grade
8. Muffle Furnace:
   Thermolyne Series 403,
   Model F 30420, F 30428
   capable of 1000°C;
   programmable.
9. Balance: Four place capability.
10. Shatter Box:
    Model # 8500, SPEX Industries Inc.
    Edison, New Jersey, USA
    Lithium Metaborate Spectromelt A20, EM Reagents.

SAMPLE ANALYSIS:

Sample Considerations:

Amount Required:	1 g
Properties:	Fresh or spent catalyst.
Interferences:	Spent catalyst must have been previously cleaned by undergoing a hot toluene reflux for at least four hours. Be aware of the possibility of auto-ignition during the drying stage. This can affect ash values.
Destructive	Yes

Preparation of Calibration Standards:

1. The standards are prepared from commercially available stock solutions. (Spex or Fisher aqueous ICAP standards).
2. The stock solution is either 500 or 1000 ppm in a dilute nitric acid matrix. Standards are purchased from the following suppliers:

   Fisher Chemicals, Fair Lawn, New Jersey, USA

   Spex Industries Inc., Edison, New Jersey, USA
3. In addition, 50 mL of concentrated nitric acid and 0.3000 g of lithium metaborate are added to each flask. Each is diluted to volume with de-ionized water.
4. An NBS coal fly ash (1633A) is routinely run as a sample to check on the precision and accuracy of both the analysis and sample preparation.

Spent Catalyst:

All spent catalyst, regardless of manufacturer, is cleaned of hydrocarbon residue by refluxing with toluene for several hours. The catalyst is dried in a 110°C oven overnight. The clean dry catalyst is shattered (<44 μ) and the powder is ashed at 725°C for a period of 16 hours. The sample is cooled in a vacuum desiccator before the final weight determination used in the Loss-On-Ignition calculation.

Fresh Catalyst:

1. Hydrotreating catalyst is shattered to <44 μ. The powder is ashed at 400°C for four hours. The sample is then allowed to cool in a vacuum desiccator before the final weight is recorded.
2. Hydrocracking catalyst is shattered to <44 μ. The powder is ashed at 538°C for a period of four hours. The sample is then allowed to cool in a vacuum desiccator before the final weight is recorded.

PROCEDURE:

1. Weigh out approximately 1 g of a homogeneous catalyst sample and place it into the shatter box.
2. Shatter the sample into a fine powder (< 44 μ) for at least one minute.
3. Place the total shattered sample into a pre-weighed porcelain crucible and weigh (crucible has previously been heated to 110°C for 30 minutes, and cooled to room temperature in a desiccator).
4. Ash the sample in a muffle furnace at 538 or 400°C (according to the sample type) for four hours.
5. Allow the sample to cool to room temperature in a desiccator.
6. Re-weigh the sample and crucible to obtain the percent ash.
7. Weigh 100 mg of ash and 300 mg of $LiBO_2$ (lithium metaborate) into a platinum crucible. Stir until homogeneous.
8. Fuse the mixture for 30 minutes at 1000°C.
9. Remove the crucible from furnace, let cool for about three minutes in air, and add approximately 10 mL of hot, 20%, HNO_3 (nitric acid) to the melt for dissolution. Magnetically stir for about five minutes.
10. Quantitatively transfer the solution to a volumetric flask (100 mL).
11. Return the crucible to the muffle furnace for 10 minutes at 1000°C.

12. Remove from furnace, allow to cool, and if any sample remains, add another 10 mL of hot 20% nitric acid and stir again for five minutes.
13. Repeat steps above until there is no sample remaining in the crucible. The above three steps should be performed at least twice.
14. Dilute to volume in volumetric flask with distilled water.
15. Remove an aliquot and dilute by a factor of 5 with distilled water.
16. Set up the instrument to include the use of the ARL V Groove Maximum Dissolved Solids Nebulizer (V MDSN).
17. Instrumental settings typically are:

Power	1200 watts
Reflected Power	< 5 watts
Nebulizer	ARL V Groove MDSN
Nebulizer Pressure	30 psi
Spray Chamber	ARL Mini-chamber
Peristaltic Pump/Nebulizer Feed Tubing	PVC 1.52 mm I.D.
Observation Height	17 mm above top coil
Coolant Gas Flow	12 L/min
Plasma Gas Flow	0.8 L/min
Sample Gas Flow	0.5 L/min
Sample Uptake Rate	2.2 mL/min

18. Aspirate sample into ICAP-AES for analysis.
19. After every three to four samples, submit a control sample to monitor instrument drift. The coal fly ash sample, from NBS, can be used to monitor the system accuracy. If deviation is greater than 2% in terms of either accuracy or precision, check the instrument calibration.
20. Periodically monitor flow rates and sample uptake rates, as a system diagnostic, during the analysis. Look for deviations greater than 5% and correct if necessary.

CALCULATIONS: Percent compositions are obtained through the following calculations:
Percent ash in sample:

$$\% \ ash = \frac{weight \ of \ sample \ after \ ashing}{weight \ of \ original \ sample}$$

Percent metal in ash:

$$\% \ Fe, \ Ni, \ V, \ Al, \ Co, \ Mo = \frac{(sample - blank)}{ash \ wt} \times CF \times 100$$

where: sample – PMT* response to sample emission line
blank – PMT response to blank emission line
ash wt – weight of ash dissolved into 100 mL (g) (0.1000 g)
CF – calibration factor ((grams metal std.)/PMT response)
PMT – response is usually in terms of counts (digitized analog voltage)
* – Photomultiplier tube

REPORT FORMAT: Results are reported in three categories:

- "0.0" below detection limits
- "TRACE" within a factor of 10 of detection limit

"NNN" quantitative value reported to three significant figures (not strictly applicable at lower concentrations).

PRECISION: Instrument Precision:

The precision of this analysis, defined in terms of percent relative standard deviation of a single series of 10 burns of a single sample, should be less than 2%. Typical precision is between 0.5–1% and is dependent on the element monitored.

Method Precision:

The precision of this analysis, defined in terms of percent relative standard deviation of a series of fresh catalyst samples individually prepared and analyzed, was found to be typically within 3% relative.

ACCURACY:

1. The accuracy of this analysis is determined by comparison with external laboratories and internally-analyzed samples of known composition.
2. Analysis results should be accurate to within 2% relative.

Measurement of Catalyst Crush Strength

SCOPE: This method measures the minimum applied force required to crush dry catalyst pellets.

SUMMARY: Catalyst pellets are dried in an oven and cooled in a desiccator. At least 50 of the cooled pellets are withdrawn for testing. The length of a single pellet is measured by a digital-reading micrometer, and the pellet placed on the platform of a force gauge. The platform is raised by means of a geared motor drive which forces the pellet against an "anvil" connected to the underside of the meter. The force is thus transferred to the meter via the pellet. As the platform continues to approach the anvil, a point is reached at which the pellet fails mechanically and the applied force abruptly declines. The meter records the force at this point of failure.

BACKGROUND: Catalyst pellets for use in a reactor tower must be sufficiently strong not to collapse under their own weight. This self-support is necessary to leave channels in the catalyst bed through which the reactants can percolate.

SAFETY CONSIDERATIONS:

1. The metals in catalyst can be harmful. Wear disposable gloves.
2. Crushed catalyst is dusty. Wear a face mask.

APPARATUS, REAGENTS, AND MATERIALS:

1. Ametek motorized test stand, Model 100.
2. Ametek Accuforce III digital force gauge.
3. Feeler gauges, 0.5 mm to 0.8 mm in 0.05 increments.
4. Digimatic precision length gauge, Mitutoyo Corporation.
5. 3M 8710 dust masks.

PROCEDURE: If the catalyst type has been tested before, necessary information on drying time and temperature, and feeler gauge gap will be in Table 1.

If the catalyst type is being tested for the first time, it will be necessary to determine these values for the new catalyst, and add them to Table 1. Details for doing this are given at the end of this Method.

Table 1.

Catalyst	Supplier	Minimum plate separation (mm)	Drying procedure
GR-12	Grace	0.75	538°C/2 h
KF-840 A-940	AKZO Chemicals	0.75	200°C/2 h
TK-561	Haldor Topsoe	1.00	200°C/2 h
C-424/ S-424 (1/16")	Criterion	0.90	200°C/2 h
C-424 (1/8")	Criterion	2.30	200°C/2 h

FOR CATALYST TYPE ALREADY LISTED IN TABLE 1:

1. Pour catalyst pellets into a porcelain dish and heat in an oven. The time and temperature of heating for different catalyst types are given in Table 1.
2. Cool and store the dried pellets in a vacuum desiccator.
3. Switch on the motorized test stand. Allow five minutes for warm-up.
4. Switch on the Accuforce gauge.
5. Turn the speed control of the test stand to maximum.
6. Consult Table 1 for the appropriate feeler gauge for the catalyst.
7. On the Accuforce gauge, press
   ZERO
   PEAK (OFF)
   UNITS to display pounds
8. The platform should be at its lowest position; if not, press the DOWN position of the manual switch to lower the platform.
9. Press the UP position of the manual switch to raise the platform.
10. After the platform has stopped, place the feeler gauge between the platform and the "anvil." If the gauge reading is not between 0 and 1 lb, turn the platform height adjustment screw and repeat above procedure until the reading is within this range.
11. Take one pellet. Measure its length in millimetres with the Digimatic precision length gauge. Record the length.
12. Lower the platform.
13. Place the measured pellet at or near the centre of the platform of the test stand.
14. Set the switches on the Accuforce gauge to
    PEAK ON
    CLEAR
15. Raise the platform by pressing UP on the manual switch.
16. When the platform stops, record the peak force.
17. Reset peak value to 0 by pressing CLEAR.
18. Sweep the dust and crushed fragments from the platform with a brush.
19. Subject a total of 50 pellets to length measurement and crush force, recording the results.

CALCULATIONS:

Calculate the crush strength for each pellet:

$$\textit{Crush strength (lb/mm)} = \frac{\textit{Peak force (lb)}}{\textit{Length of pellet}}$$

Calculate the average crush strength:

$$\textit{Average crush strength (lb/mm)} = \frac{\textit{Sum of individual crush strengths}}{\textit{Number of pellets crushed}}$$

For new catalyst types:

1. Determining the appropriate gap for new catalyst types:

   The platform must travel close enough to the anvil to thoroughly crush the pellet, but must not continue travelling to the point that the crushed material becomes compacted. If this were to happen, force higher than the crush strength would be transmitted to the anvil through the compacted material.
2. All pellets of the same catalyst type are assumed to be identical in diameter.
3. Dry the catalyst for a length of time and at an oven temperature setting agreed to by the catalyst suppliers.
4. Measure the diameter of a pellet using the Digimatic precision gauge.
5. Set the OFF switch of the motorized test stand to leave a minimum gap between platform and anvil (at the highest point of platform travel) of slightly less than the pellet diameter. Record this gap setting.
6. Measure the length of a pellet using the Digimatic precision gauge.
7. Place the pellet on the platform.
8. Activate the test stand cycle.
9. Record the peak force.
10. Repeat for a total of 10 pellets at that gap setting.
11. If all the pellets are crushed at this gap setting, record the setting in Table 1.
12. If any pellets remain uncrushed, reduce the minimum gap by 0.1 mm and repeat the test for 10 more pellets.
13. Repeat at progressively lower final gap settings until an entire batch of pellets is crushed. Enter the gap setting in Table 1.

PRECISION: Six determinations for one lot of Grace GR-12 yielded an average crush strength of 1.64 lb/mm with a standard deviation of 0.09 lb/mm.

REFERENCE: J.T. Bulmer, T. Everett, D. Appelt, New Method, adapted from W.R. Grace 5.3.00.161, Nov. (1989).

Determination of Loss on Attrition of Fresh Hydrocracking Catalyst

INTRODUCTION: Loss on attrition (LOA) provides a measure of the friability of a catalyst and hence its tendency to produce fines as a result of transportation, handling, and fluidization in a reactor.

SCOPE: This method determines the loss on attrition of fresh hydrocracking catalyst.

SUMMARY: Fresh catalyst is screened to remove fines, dried, and then introduced into a tumbling apparatus where it is rotated at 60 rpm for 22 hours (79,200 revolutions). The sample is screened and dried again. The difference between the weight of screened catalyst introduced into the drum and the weight of screened catalyst after tumbling is the loss on attrition. A calculation gives the result as a percentage.

BACKGROUND: This method is based on ASTM D 4058-87 but also reflects experience with hydrocracking catalysts and their suppliers. The values determined by this method are dependent on the specifics of the procedure. Consequently, results are interpreted by comparison with other materials treated in an identical manner. Specifics of the method to give precise data are:

1. Prolonged attrition of 79,200 revolutions versus 1800 revolutions in ASTM D 4058.
2. Automatic shut-off after a preset number of revolutions.
3. The calculations include an arbitrary convention of converting the results from a 22 to a 24 hour basis. This convention is of trivial significance since interpretation compares data obtained in an identical manner.
4. The method assumes that a 100 g sample of catalyst has been submitted or prepared by riffling.

SAFETY CONSIDERATIONS: Catalyst: consult Material Safety Data Sheet.

APPARATUS, REAGENTS, AND MATERIALS:

1. Tumbling apparatus including a stainless steel drum with baffle as per ASTM D4058. Elements of the apparatus are: motor, roller, drum with lid, tachometer, counter, and guard. The outside of the drum has 30 evenly-spaced teeth to activate the proximity switch for rpm measurement and one tooth for the counter. An example list of components includes:
   - Baldor Motor CDP-3310
   - Leeson Speedmaster Motor Controller
   - Omron H7ER-SBV Tachometer
   - Omron H7ER-BV Counter
   - Omron E2E-XSEl Proximity Switches for tachometer and counter
   - Omron G4B-112Tl-C-US Solid State Relay
2. Sieve, 28 mesh (600 µm), 200 mm diameter, with pan and lid.
3. Balance, top loading, readable to 0.01 g.
4. Wrench to tighten lid to drum.
5. Vacuum desiccator with type 4A molecular sieve as desiccant.

6. Brush, 25 mm width.
7. Muffle furnace.
8. Evaporating dish, porcelain, 250 mL.

SAMPLE CONSIDERATIONS:

Amount Required: 100 mL
Destructive: Yes

PROCEDURE:

1. Sieve the sample over a 28 mesh screen.
2. Heat the +28 mesh portion of the sample in a porcelain evaporating dish in a muffle furnace for four hours at 538°C. Allow the sample to cool in a vacuum desiccator containing activated type 4A molecular sieve.
3. Quickly weigh the cooled catalyst to 0.01 g, place in the drum of the tumbling apparatus and fasten the lid to the tumbler.
4. Place the drum in the tumbling apparatus. Ensure the motor controller is set to 60 rpm and the revolutions counter is set to 79200. Place cover over apparatus and turn on the tumbling apparatus. Allow sample to be attrited until tumbling is terminated by the revolution counter.
5. Remove lid from tumbler drum. Remove the attrited catalyst using a brush.
6. Screen the attrited catalyst using a 28 mesh sieve. Dry the +28 mesh portion in an evaporating dish in a muffle furnace for one hour at 538°C.
7. Cool the catalyst in a desiccator and re-weigh.

CALCULATIONS:

Percent loss-on-attrition is obtained by the following calculation:

$$\% \text{ Loss-on-attrition} = \left[\frac{\text{Original screened sample weight} - \text{Attrition screened sample weight}}{\text{Original screened sample weight}}\right] \times \frac{24}{22} \times 100$$

REPORT FORMAT:

Report as percent loss-on-attrition (LOA).

PRECISION:

Example precision determined on two sets of equipment for a hydrocracking catalyst are shown in Table 1.

Table 1. Precision on two assemblies

	N	Mean% LOA	Standard deviation
Assembly A	10	1.51	0.46
Assembly B	9	2.44	0.73

TIME CONSIDERATIONS:

Time Per Analysis: ~35 h (includes drying time)
Technologist Contact Time: ~1 h

REFERENCE:

ASTM Method D 4058, "Attrition and Abrasion of Catalysts and Catalyst Carriers."

Determination of Compacted Bulk Density of Catalyst

INTRODUCTION:

Bulk density for a catalyst is the sample mass divided by the volume occupied by catalyst and voids. With this definition, bulk density depends on the extent of packing of the sample. Compacted bulk density is a bulk density performed in compliance with a specified manner of mechanically enhancing particle packing. Compacted bulk density is frequently included in fresh catalyst specifications.

SCOPE:

This method determines the compacted bulk density of catalyst.

SUMMARY:

Approximately 100 g of fresh catalyst is dried at 400°C for three hours. The cooled, dry sample is poured into a 100 mL graduated cylinder and immediately weighed. The graduated cylinder is tapped on a tapping apparatus for two minutes. The final catalyst volume is recorded and used to calculate the compacted bulk density.

BACKGROUND:

1. For reactors of fixed volume, the extent of catalytic ability present is related to the mass of catalyst. On the other hand, sufficient void volume must be present to allow passage of reacting fluids. Compacted bulk density measures the ratio of catalyst mass to the volume occupied when the catalyst is compacted in a bed.
2. Related methods may refer to apparent bulk (1), vibrated apparent packing (2), vibratory packing (3), and tap (4) density.
3. The method assumes that a 100 g sample of catalyst has been submitted or prepared by riffling.

SAFETY CONSIDERATIONS:

Catalyst: consult Material Safety Data Sheet.

APPARATUS, REAGENTS, AND MATERIALS:

1. Vanderkamp Tap Density Tester, equipped with cams to provide a 3.2 mm drop.
2. Acoustic cabinet for the Vanderkamp Tap density Tester.
3. Balance, top loading, readable to 0.01 g.
4. Graduated cylinders, 100 mL.
5. Vacuum desiccator with type 4A molecular sieve as desiccant.
6. Feed funnel (2).
7. Muffle furnace.
8. Evaporating dish, porcelain, 250 mL.

SAMPLE CONSIDERATIONS:

Amount Required: 100 g
Destructive: No

PROCEDURE:

1. Place the sample in an evaporating dish and dry at 400°C for three hours.
2. Cool the sample in a vacuum desiccator containing activated type 4A molecular sieve.
3. Weight the graduated cylinder.

4. Using a feed funnel, pour the dry sample into the graduated cylinder and immediately weigh the cylinder and sample.
5. Place the graduated cylinder on the platform of the Vanderkamp tap density tester and rotate to lock in place.
6. Set the number of taps on the tap density tester to 600.
7. Turn on the tap density tester and close the door to the acoustic cabinet.
8. When the counter stops operation of the tap density tester, turn the graduated cylinder to unlock the base and remove the cylinder from the platform.
9. Tap the graduated cylinder gently to settle the top layer of catalyst and determine the volume of settled catalyst.

CALCULATION:

$$\textit{Compacted bulk density (g/mL)} = \frac{\textit{Weight of sample}}{\textit{Settled volume of sample}}$$

PRECISION: 21 lots of LC-Finer catalyst supplied by Grace gave an average compacted bulk density of 0.56 g/mL. The standard deviation was 0.029 g/mL.

TIME CONSIDERATIONS:

Time Per Analysis (excluding drying time):	4 min
Technologist Contact Time:	2 min

Length and Diameter of Catalyst

INTRODUCTION: Specification on the manufacture of extruded catalysts include distribution for the particle lengths and diameter. The data may be interpreted in terms of quality control on manufacture, packing, and performance in a fluidized bed.

SCOPE: This method describes the determination of length and diameter for extruded catalysts.

SUMMARY: Length and diameter of about 150 catalyst particles are measured using digital callipers. The data are reported as an average length and diameter.

BACKGROUND:

1. The method described here reports an average length and diameter for a subsample of extruded catalyst. In practice the specifications for a catalyst supplier may also include acceptable percentages of particles in ranges of length and/or diameter. The data would then be reported in a format consistent with the specifications. In fact the equipment described here includes provision for setting upper and lower limits for characterizing the data. The number of particles selected for measurement in the present method is 150. This number may be adjusted and is governed by the nature of the specifications.
2. The equipment for determining length and diameter by calliper is inexpensive. However, the procedure is labour intensive. An alternative is the use of image analysis which requires more expensive equipment. Development of an image analysis sizing technique requires selection of appropriate illumination (e.g., back ring lighting) to eliminate shadows, magnification, and feature parameters.
3. Duplicate measurements on a set of extruded catalyst particles have demonstrated that the particle length can be reduced by handling and the measurement process. Careful handling of the particles is required to minimize these size reductions.

SAFETY CONSIDERATIONS: Catalyst: consult Material Safety Data Sheet.

APPARATUS, REAGENTS, AND MATERIALS:

1. Digital Callipers: Mitotoyo 0.01–150 μm with output cable.
2. Mitotoyo Digimatic Mini processor DP-1DX.
3. Disposable gloves.

SAMPLE CONSIDERATIONS:

Amount Required: At least 150 particles
Destructive: No

PROCEDURE:

1. Measure all particles using the callipers,
   - For trilobe pellets, ignore one long or short lobe and measure the average of the other two.
2. For length
   a. grasp the pellet by the end, making sure not to sink calliper jaws into the pellet;

b. grasp the pellet in such a way as to give the average length of the pellet, not the maximum or minimum.

3. For diameter
   a. Grasp the pellet across the diameter, perpendicular to the edges, closing the jaws just enough for the pellet to be picked up.
   b. For trilobe pellets, grasp the pellet so that two lobes are flat against one jaw, and with the other lobe flat against the other jaw. Press DATA while holding callipers at proper size. Repeat until all pellets are measured (if a value is entered erroneously, press CE to clear the last data point).
4. Press STAT to have calculations performed. After printout is finished, press CL to clear the memory for the next sample.
5. Connect the callipers to the mini-processor with the interface cable. Switch on the mini-processor.
6. Turn on power to the callipers ("ON/ZERO" button). Set the callipers to read in millimetres ("IN/MM" button). Zero the callipers with the jaws closed ("ON/ZERO" button).

   If no mini-processor is available, pellet measurement and the calculation may be performed manually.

CALCULATIONS:

1. Length:

$$\text{Average length} = \frac{\text{Sum of lengths (mm)}}{\text{Number of pellets}} \text{ (given on the mini-processor printout)}$$

2. Diameter:

$$\text{Average diameter} = \frac{\text{Sum of diameters (mm)}}{\text{Number of pellets}} \text{ (given on the mini-processor printout)}$$

PRECISION: Duplicate determination of the length of 80 cylindrically shaped extruded (1 to 6 mm in length) yielded a standard deviation of 0.050 mm.

TIME CONSIDERATIONS: Time Per Analysis: 30 min total (length and diameter)
Technologist Time: 30 min

Determination of the B.E.T. Surface Area by the Continuous Flow Method

INTRODUCTION: The catalysts used in hydrocracking and hydrotreating are porous with extensive pore structures and high surface areas. The determination of surface area based on the multi-layer adsorption theory of Brunauer-Emmett-Teller (B.E.T.) provides a characterization of fresh, spent, and regenerated catalysts that can be related to performance.

SCOPE: This method measures B.E.T. surface area for catalysts having a surface area greater than 5 m^2/g.

SUMMARY: Catalyst is outgassed by heating in a helium purge. Outgassing removes contaminants, e.g. water, from the catalyst pores. Gaseous mixtures, containing 10, 20, and 30 mol-% nitrogen, respectively, are passed over the catalyst which is cooled with a liquid nitrogen bath. Under these conditions, nitrogen adsorbs on the catalyst surface. Adsorption is complete when a thermal conductivity detector comparing the composition of the gas entering and exiting the sample cell gives a constant signal. The sample is then heated to ambient temperature which causes the nitrogen to desorb. The volume of nitrogen released is measured by the thermal conductivity detector. The system is calibrated using a known volume of pure nitrogen. Calculation of the B.E.T. surface area is based on the volume of nitrogen adsorbed by the three nitrogen mixtures as well as the sample weight, ambient temperature, and barometric pressure.

BACKGROUND:

1. The effectiveness of catalysts for hydrotreating and hydrocracking is dependent on the catalyst surface area and pore structure. Consequently, these parameters are measured for quality control of supplied materials and to monitor changes during use. Two techniques are commonly used to quantify catalyst surface area and pore structure: nitrogen adsorption and mercury porosimetry. The techniques are explained elsewhere (1,2).
2. A nitrogen adsorption isotherm is a plot of the volume of nitrogen adsorbed on a sample surface at constant temperature versus the relative pressure P/P_o where P is the equilibrium pressure of the adsorbate and P_o is the saturation vapour pressure. The constant temperature used for the measurement is the boiling point of the adsorbate. Data for P/P_o between 0.05 and 0.35 is used for the B.E.T. surface area calculation. At higher P/P_o values, both adsorption (filling pores) and desorption (emptying pores) isotherms can be recorded and interpreted in terms of a pore size distribution. The method described here can be extended to record the isotherm at higher P/P_o; but the procedure is long and tedious. Syncrude productivity requirements have resulted in the recent purchase of automated equipment for both nitrogen adsorption and mercury porosimetry.
3. Surface area determinations by the continuous flow method have been used by Syncrude for over 10 years. It is reasonably inexpensive, reliable, and well-suited to situations requiring modest productivity. It measures three points on the nitrogen adsorption isotherm for the catalyst sample and calculates a surface based on the model described by the Brunauer-Emmett-Teller (B.E.T.) equation. Related methods are described by Universal Oil Products (UOP) methods 425-86, 821-81, and ASTM D3663-84, D4567-86.

SAFETY CONSIDERATIONS:

1. Dewar flask: implosion hazard.
2. Liquid nitrogen: contact of liquid nitrogen with the skin can cause injury by severe freezing. Wear gloves and eye protection.
3. Catalyst: consult Material Safety Data Sheet.

APPARATUS, REAGENTS, AND MATERIALS:

1. Quantasorb sorption system (model QS-7) equipped with chart recorder, sample cell, heating mantle, and Dewar flasks, and multiple sample manifold (3).
2. Quantector (3).
3. Pre-mixed primary gas standards of composition 10, 20, and 30 mol-% nitrogen in helium.
4. Nitrogen, pre-purified (99.998%).
5. Helium, high purity (>99.99%).
6. Precision gas syringes equipped with Chaney adaptors with capacities of 0.25 mL to 20 mL.
7. Analytical balance.
8. Liquid nitrogen.

SAMPLE CONSIDERATIONS:

Amount Required: 10 g
Destructive: No

PROCEDURE:

Prior to outgassing, used catalyst that has not been regenerated must be cleaned with hot toluene in a Soxhlet extractor to remove oily residues.

A. Outgassing:

1. Weigh about 0.1 g of catalyst sample and load it into a cell. Fit the sample cell into a set of "quick connect" fittings, and attach it to the Quantector. Outgas the sample under a small helium purge at elevated temperature.
2. Purge Rate:

   Place the tubing of the outgassing exit in a beaker of water and set the purge at about one bubble per second.
3. Temperature:

   Appropriate for catalyst type under investigation. A common value is 160°C.
4. Outgassing Time:

   At least four hours. It is convenient to outgas overnight or to monitor contaminants with the detector.

B. Preparation of the Quantasorb:

1. Purge the Quantasorb and manifold for several minutes with the 10% nitrogen/helium. The rate of flow through each sample cell of the multiple sample manifold should be 20 mL/min. This requires an empty cell connected at each manifold position.
2. Raise a Dewar of liquid nitrogen to surround the Quantasorb cold trap.

3. Ensure that gas flow is being directed through one of the sample cell locations of the manifold to the detector of the Quantasorb.
4. Switch on the Quantasorb and set it to a bridge current of 150 mA.
5. Allow the instrument to stabilize approximately 20 minutes (i.e., achieve a constant signal from the thermal conductivity detector).
6. Upon completion of the outgassing, transfer the sample cell to one of the manifold cell positions. While this is being done, ensure that gas flow from one of the other cell positions is being directed to the detector.
7. After a few minutes, turn the selector valves to direct the flow through the sample cell to the detector. The flow through the other sample locations of the manifold is directed to vent.
8. Switch the COUNT/ZERO toggle to the ZERO setting and zero the signal meter using the ZERO ADJUST potentiometer. Then switch the COUNT/ZERO toggle to the COUNT setting and zero the signal meter using the COARSE and FINE potentiometer. Leave the toggle in the COUNT setting.
9. Set the threshold by turning the THRESHOLD knob counter clockwise until counting commences on the digital display (green light comes on) and then clockwise until no counts are given (green light goes out). Check this setting with the COARSE ZERO control knob. On the downstroke of the COUNTS/SEC needle, the light should extinguish approximately 1/2 scale division above zero.

C. Sample Analysis:

1. With the instrument in the ADSORB position and COUNT setting, zero the signal meter with the COARSE and FINE potentiometers.
2. Raise the Dewar to surround the sample cell with liquid nitrogen. Wait for completion of nitrogen adsorption as indicated by a return to the baseline, already established.
3. Set the attenuator such that the desorption peak is expected to be at least 50% but not more than 100% of full scale on the meter. Typically the attenuation for fresh or used catalyst is 128 or 256 depending on sample size.
4. Switch the instrument to the DESORB position and re-zero the signal meter in the COUNT position. Reset the integrator count to zero.
5. Remove the liquid nitrogen and surround the sample cell with a beaker of room-temperature water.
6. When the desorption is complete, as indicated by a return to the established baseline, the green threshold light goes out. Record the integrator value and reset to zero.
7. If the peak is less than 50% of full scale, repeat the adsorption/desorption using a lower attenuation setting. If the peak is greater than 100% of full scale, repeat the adsorption/desorption using a higher attenuation.
8. After a nitrogen desorption peak between 50 and 100% of full scale is obtained, select a volume of pure nitrogen that will give a peak height within 15% of the sample peak height. This selection of nitrogen volume is performed by consulting a previously developed plot of nitrogen volume versus percent of full scale for various attenuations.

9. For the nitrogen volume selected, insert a suitable precision gas syringe into the OUT septum of the Quantasorb and flush it three times with nitrogen. Withdraw the selected volume of nitrogen and inject it slowly into the IN septum of the manifold adjacent to the sample cell. Do not let the sample rotameter go off scale during the injection. Record the volume of nitrogen injected.
10. After the green THRESHOLD light goes out, record the integrator value corresponding to the calibration signal.
11. If samples at other sample stations of the manifold are to be analyzed, direct the gas flow for the desired station to the detector while all other gas flows are directed to vent.
12. Repeat the above sample analysis for each sample and each nitrogen/helium gas mixture.
13. Record the barometric pressure and room temperature at the time of measurement.
14. When all measurements are complete, turn the bypass valve of the Quantasorb to the cell bypass position. Remove the sample cells from their fittings. Transfer the catalyst samples to tared beakers and immediately determine the weight of sample to 0.1 mg.

D. Shutdown Procedure:

1. Turn off power,
2. Stop gas mixture flow and immediately remove liquid nitrogen from cold trap.
3. Remove and clean the cold trap cell.
4. Shut off helium, nitrogen, and 10, 20, and 30 mol-% nitrogen at the cylinders.

E. Preparation of Calibration Gas Plot:

1. To aid in determining the amount of nitrogen gas to inject into the Quantasorb in the detector step, a plot is made of Volume Nitrogen Calibration Gas versus percent of Chart Scale.
2. This plot is a general guide and can be made once a year, or when detector response begins to change.
3. Purge the Quantasorb and manifold for several minutes with 10% nitrogen/helium. The flow through each cell position of the manifold should be 20 mL/min. This requires an empty cell connected at each manifold position.
4. Raise the Dewar of liquid nitrogen to surround the cold trap.
5. Ensure that gas flow is being directed through one of the sample cell locations of the manifold to the detector.
6. Switch on the Quantasorb and set it to a bridge current of 150 mA. Allow the instrument to stabilize, i.e., achieve a constant signal from the thermal conductivity detector.
7. Switch the COUNT/ZERO toggle the ZERO, and zero the signal meter using the ZERO ADJUST potentiometer knob. Then switch the COUNT/ZERO toggle to the COUNT setting and zero the signal meter using the COARSE ZERO and FINE ZERO potentiometer knobs. Leave the toggle in the COUNT position. Set the threshold

by turning the THRESHOLD knob counterclockwise until no counting commences (green light comes on) and then clockwise until no counts are given (green light goes out). Check this setting with the COARSE ZERO control knob. On the downstroke of the needle, the light should extinguish approximately 1/2 a scale division above zero on the counts second scale.

Then:

a. At an attenuation of 64, use a precision gas syringe to inject 0.5 mL of pure nitrogen into the septum in the sample manifold having the toggle directed to detector.

b. A peak will be traced out on the chart recorder. Record the percent of chart scale for this volume of calibration gas.

c. After the peak comes down to baseline, repeat this procedure for 0.75 mL, 1.0 mL, 1.5 mL, and 2.0 mL of nitrogen. Plot Nitrogen Calibration gas volume versus percent of Chart Scale for this attenuation.

d. Repeat the procedure from Step 1 for attenuations 128, 256, and 512. The volumes of calibration gas vary with the attenuation setting as follows:

Attenuation	Volume nitrogen (mL)
128	0.5, 1.0, 1.5, 2.0, 2.5
256	2, 3, 4, 5, 6
512	5, 7, 9, 10

CALCULATIONS:

1. The relative pressure at each data point is given by:

$$\frac{P}{P_o} = \frac{\left(C_{N_2}\right)_f P_a}{\left(P_a + 15\ mm\right)}$$

where: $(C_{N_2})_f$ = mole fraction of nitrogen in the carrier stream
P_a = barometric pressure in mm Hg .

2. Calibration gas weight:

$$X_c = \frac{P_a \left(M_a\right) V_c}{6.235 \times 10^4\ T}$$

where: X_c = weight of nitrogen corresponding to the calibration volume (g)
P_a = barometric pressure (mm Hg)
M_a = molecular weight of adsorbate (28.01 g/mol for nitrogen)
V_c = calibration volume (mL)
T = room temperature (K)
6.235×10^4 = gas constant (appropriate units)

3. The weight of nitrogen absorbed on the sample at a given data point is given by:

$$X = \frac{(A)\ X_c}{A_{CAL}}$$

where: X = weight of nitrogen absorbed on the sample (g)
A = signal area
X_c = weight of nitrogen corresponding to the calibration volume (g)
A_{CAL} = calibration signal area

From the above quantities, $\frac{1}{X\left(P_o/P-1\right)}$ is

calculated for each data point and is then plotted against P/P_o. The slope and intercept of the plot are then recorded.

4. The weight of nitrogen adsorbed on the sample surface at a coverage of one monolayer is given by:

$$X_m = \frac{1}{S + I}$$

where: X_m = weight of nitrogen adsorbed at a coverage of one monolayer (g)
S = slope of the B.E.T. plot
I = intercept of the B.E.T. plot

5. The total surface area of the sample is given by:

$$S_t = \frac{X_m\ N\ A_{cs}}{M_a}$$

where: S_t = total surface area of the sample (m^2/g)
X_m = weight of nitrogen adsorbed at a coverage of one monolayer (g)
N = Avagadro's number (6.02×10^{23})
A_{cs} = absorbate cross sectional area (for nitrogen, 16.2×10^{-20} m^2)
M_a = molecular weight of adsorbate (for nitrogen, 28.01 g/mol)

The specific surface area of the sample is given by:

$$S = \frac{S_t}{W}$$

where: S = specific surface area (m^2/g)
S_t = total surface area of the sample (m^2)
W = weight of sample, (g)

REPORT FORMAT: Report specific surface area in m^2/g to the nearest whole number.

PRECISION: A standard deviation of 3 m^2/g was found for 12 replicate determinations of a catalyst sample with a specific surface area of 140 m^2/g.

TIME CONSIDERATIONS:

Time Per Analysis:	6 h
Technologist Contact Time:	2 h
Samples Per Time Period:	6/d
Calibration Time:	4 h (only intermittently)

REFERENCES:

1. Lowell, S., "Instruction Manual for the Quantasorb Sorption System," Quantachrome Corporation, 1978.
2. UOP Method 425, "Surface Area, Pore Volume and Pore Diameter of Porous Substances by Nitrogen Adsorption."

Pore Size Distribution and Total Pore Volume of Catalyst Materials by Mercury Intrusion

INTRODUCTION: Syncrude uses a wide variety and large amounts of catalyst, especially throughout the upgrading portion of the plant operation. Catalyst is used in both the hydrotreating and the hydrocracking operations in upgrading. Determination of the pore size distribution and the total pore volume of fresh catalyst is an important factor in the quality assurance program for a previously selected catalyst, as well as for the provision of information on a potential catalyst.

SCOPE: This test method covers the determination of the pore size and volume of catalysts by the method of mercury intrusion. The range of the apparent diameters for which it is applicable is fixed by the pre-set pressure range.

SUMMARY:

1. A sample to be tested is sealed in a penetrometer and evacuated. The penetrometer is filled with mercury while a very low pressure is maintained. Thus, mercury intrudes only the largest pores of catalyst sample. The capacitance of the system is measured at this "zero" state.
2. Pressure on the mercury is systematically increased in a step-wise manner. At each increase in the pressure, the volume of mercury in the stem of penetrometer decreases as the mercury is forced into the pores. The total surface area of the Hg capacitor plate (the Hg in the stem and the metal cladding) is reduced and the capacitance is reduced likewise. Capacitance is proportional to the volume in the stem.
3. The complete testing is done in two stages:
   a. Low pressure
   b. High pressure

   Low pressure operation measures pores with diameters from 360 to 6 μm and high pressure operation measures pores with diameters from 6 to 0.003 μm.

BACKGROUND: The evaluation of a potential catalyst for Syncrude's hydrotreating or hydrocracking plants requires a variety of analytical techniques. Two of the more important factors are the determination of the catalyst pore size distribution and pore volume. Pore sizes in the range of tens of nanometres play a very important role in defining the total surface area of the catalyst available for reaction. Typical methods for determination of the pore size distribution and pore volume include adsorption of a pure gas (N_2) into the evacuated pores or forcing under high pressure a pure non-wettable liquid (mercury) into a previously de-gassed catalyst pellet. High pressure mercury porosimetry provides more information about the very small pores than does the gas adsorption technique which is optimal for the mid-range pore sizes. In the case of mercury intrusion into the pores at pressures up to 415,000 kPa (61,000 psi) the following information can be obtained: total pore area, median pore diameter (volume and area), average pore diameter, bulk density, and apparent skeletal density. This information contributes to an estimation of the catalyst performance and provides quality assurance information for already selected catalysts.

SAFETY CONSIDERATIONS:

Warning:

1. Mercury is a hazardous substance that can cause illness and death. Always store in closed containers to control its evaporation, and use it only in well-ventilated rooms. Mercury can also be absorbed through the skin. Avoid direct contact. Wash hands immediately after any operation involving mercury. Exercise extreme care to avoid spilling mercury. Clean up any spills immediately using procedures recommended explicitly for mercury.
2. Samples that have been exposed to mercury are dangerous.

Mercury Spills:

3. Mercury spill kits should be used to collect spilled material for reclamation. All spills must be cleaned up immediately.

Storage:

4. Store mercury in approved storage area away from heat, fire hazards, or incompatible substances.
5. Wear gloves all the time when handling catalyst samples. Riffle samples in fumehood and wear a dust mask.
6. Particular care must be taken when operating high pressure equipment. Do not open the HP chamber if the high pressure light is on.

APPARATUS, REAGENTS, AND MATERIALS:

1. Micromeritics Autopore II (Model 9220).
2. Computer with printer (compatible with Micromeritics Autopore).
3. Penetrometers.
4. Mercury (analytical grade).
5. Apiezon "H" grease and high vacuum silicon grease.
6. High pressure fluid, vacuum pump fluid.
7. Hexane.
8. Isopropanol (IPA).

SAMPLE CONSIDERATIONS:

Riffle catalyst sample to 1–2 g and heat it to 532°C for at least 15 minutes. 0.8 to 1 g of sample is required for analysis.

PROCEDURE:

Calibration:

1. The instrument performance is checked against a reference material of silica alumina.
2. Recommended quantity per test: There are small differences among pellets. Between 10 and 14 pellets are needed to obtain a statistically reliable sample. A single pellet weighs about 0.05 g, so this means a sample weight of from 0.5 to 0.7 g.
3. Pertinent test conditions: Mechanical evacuation to 50 μm Hg is adequate. Use an equilibration time of 10 seconds, a contact angle of 130°, and a surface tension of 485 dyne/cm.

   Typical results are shown in Table 1.

Table 1. Typical Calibration Results

	Maximum pressure	Maximum pressure
	60,000 psia (414,000 kPa)	30,000 psia (207,000 kPa)
Total intrusion volume	0.54 ± 0.05 cm^3/g	0.33 ± 0.05 cm^3/g
Total pore area	230 ± 20 m^2/g	75 ± 10 m^2/g
Median pore diameter (volume)	0.010 ± 0.001 µm	0.03 ± 0.005 µm
Median pore diameter (area)	0.005 ± 0.002 µm	0.010 ± 0.002 µm

SAMPLE ANALYSIS:

1. Assure that Main Power Switch is on, computer, instrument fan, and cleaning station fans running.
2. Check mercury level in reservoir; it should be within one-half to one inch from the top.
3. Check high pressure oil level in High Pressure chamber; the oil level should be up to "E" mark as indicated in the manufacturer's documentation.
4. Check vacuum pump oil level. Vacuum pump has a visual oil level indicator. The indicator is visible upon opening the instrument door.

Low Pressure:

1. Riffle catalyst sample to 1–2 g and heat it to 532°C for at least 15 minutes. 0.8 to 1 g of sample is required for analysis.
2. Select proper, clean, and dry penetrometer (see Manufacturer's Application Note for penetrometer selection).
3. Grease the lip of the penetrometer with Apiezon H grease.
4. Assemble and weigh the empty penetrometer and record the weight on the worksheet. Record all other information as required, such as PNTR Vol., etc.
5. Remove the penetrometer assembly and remove grease from all surfaces using hexane.
6. Using care, place the hot catalyst sample into the penetrometer and quickly grease and seal it.
7. Assemble and weigh the penetrometer, and record the weight on the worksheet.
8. Use a nylon spacer on a 3 mL penetrometer before mounting, and grease the end of penetrometer using high vacuum silicon grease. Avoid getting grease into the stem opening.
9. Mount penetrometer in Low Pressure port.
10. Install a metal rod into all unused ports.
11. Tighten the seals firmly.
12. Place capacitance transducers on the penetrometer and lock in place, verifying contact by noting a change in INTVOL reading on status display.
13. Select Main Function Key Menu item F5; Sample Data Menu screen will appear. Select F3 (CREATE SAMPLE DATA) and fill in the requested data. A CREATE SAMPLE DATA screen must be completed for each sample.

14. Select Main Function Menu item F6 to start low pressurization, and complete the screen.
15. After completion of Low Pressure run screen, press Pg Dn to initiate the run, and then press F2 for Main Function Menu. STATUS RUN SCREEN can be selected to monitor the run condition."
16. Monitor the status display; it will indicate IDLE in the LP field when the run is finished.
17. At the end of the Low Pressure run, carefully remove the mercury-filled penetrometer from the LP port, and keep the open end of the penetrometer in an upright position at all times to prevent mercury loss.
18. Remove the nylon spacer and grease from the stem.

High Pressure:

1. Weigh the penetrometer filled with sample and mercury, and record the weight on the worksheet.
2. Insert the penetrometer into the High Pressure chamber. The penetrometer should be in the centre of the High Pressure chamber, with the sample bulb down.
3. Make sure the vent valves are open. Close the High Pressure chamber.
4. When lowering the High Pressure-chamber head, slowly turn the head into the chamber until oil starts flowing into the plastic reservoir on top of the vent valve, to release any air bubbles trapped in the chambers. Note the pressure reading on the status display. It is important that you continue to turn the heads slowly so that you don't inadvertently generate pressure above ambient.
5. Use Main Function Menu F5 and F4 to EDIT the sample data screen to enter with weight of the penetrometer containing the sample and mercury.
6. Complete the "Start High Pressure Run" screen by choosing F7. Be sure that the sample number is matched with the correct port and the appropriate pressure table number is used. High Pressure runs are not possible unless valid Low Pressure runs are completed under specified sample identification numbers.
7. To initiate a High Pressure analysis, press Pg Dn while "Start High Pressure Run" screen is being displayed.
8. Close both vent needles at this time by turning clockwise.
9. Start another Low Pressure run if desired. Simultaneous overlapping Low and High Pressure runs can be performed. The Status Display will indicate IDLE in the HP Field when the High Pressure run is completed.
10. Remove and clean the penetrometer after the High Pressure run is completed.
11. Pore diameter sizes are μm in the printed report. We use Angstrom (Å) unit for reporting purposes (0.4 μm = 4000Å).
12. Volumes of Hg Pore Size Distribution of >250Å, >500Å, >5000Å, and >4000Å are reported (Pore Size versus Cumulative Volume).

CALCULATIONS: All calculations are performed by the computer controlling the instrument.

REPORT FORMAT: A report is automatically printed at the end of the High Pressure run. This report gives the intrusion data summary and pore size distribution of catalyst. From intrusion data summary, total intrusion volume (HP PV Total) is reported. Pore size distribution results are found in the Pore Diameter section. Pore volume results are found in the Cumulative Volume section.

PRECISION AND ACCURACY: Precision:

Intrusion Volume: ±0.05 cm^3/g 10% RSD

Pore Area: ±20 m^2/g at 60,000 psia (414,000 kPa).

ACCURACY: Instrument is calibrated to within ±0.05 on manufacturer's standard sample.

TROUBLESHOOTING:

1. If the results vary widely from the expected values, repeat the analysis. First check the value of "Stem Volume Used" in the printed report under the heading of Intrusion Data Summary. A percent stem reading of less than 25% or more than 90% suggests the need for a procedural change. The first instance suggests that a larger quantity of sample might give better resolution, and the second indicates that the capillary is on the verge of being depleted.
2. Improper sealing of penetrometer into their preparation ports is most suspect when difficulty in encountered in attaining adequate vacuum conditions. Test this possibility first by tightening further the knobs controlling these sealing mechanisms.
3. Difficulty in evacuating a sample or a rather abrupt decay in the vacuum system during sample evacuation can be due to scratches or other imperfections in either of the two surfaces sealed with vacuum grease. Removal of scratches is readily accomplished by polishing with 600-grit emery paper.
4. Warning Buzzer: the buzzer's sounding indicates that mercury has been improperly drawn into the protecting trap. It is drained by removing the plug extending down from the trap. This plug is reached through the front door. As the instrument is faced, the plug is around in the upper, back, right-hand corner. Be sure to position a container beneath the trap before the plug is removed.

Determination of Surface Area, Nitrogen Pore Volume, and Pore Size Distribution of Catalyst by Micromeritics ASAP 2000

INTRODUCTION: Syncrude uses various types and amounts of catalyst throughout the upgrading process. An important specification for this catalyst is the total surface area and pore volume available for interaction with the feed. The pore size distribution is also an important consideration. This information can be obtained by monitoring the adsorption and desorption of nitrogen gas onto the catalyst.

SCOPE: This method describes the determination of surface area, nitrogen pore volume, and pore size distribution by gas adsorption.

SUMMARY:

1. Measurement of surface and pore size by ASAP 2000 is based upon the physical adsorption and desorption of gas (typically nitrogen) at the surface and in the pores of solid sample.
2. A surface area measurement requires that first the catalyst in question be free of gases and vapours that are acquired from exposure to the atmosphere. This usually is done by heating and evacuating the catalyst (de-gassing). The catalyst is then cooled to an ambient temperature and backfilled with nitrogen.
3. The catalyst is exposed to the adsorbate gas (nitrogen) in a series of controlled pressure increases, and the equilibrium quantities of gas adsorbed are determined for each pressure. The gas volume adsorbed at each pressure defines an isotherm. One can determine from the isotherm the quantity of gas needed to cover the solid surface, both external surface and internal surface (with the pores having openings to the surface), with a monolayer of close-packed adsorbate molecules. The area of catalyst on a molecular scale is calculated using the projected area of each adsorbed gas molecule.
4. The characteristic pore size and volume distribution or pore structure of a material can also be quantified by gas adsorption. The ASAP 2000 performs both DIGISORB and BJH calculation protocols on both absorption and desorption data.

BACKGROUND: The characterization of catalyst used by Syncrude includes the determination of total surface area, pore volume, and pore size distribution. Nitrogen porosimetry and high pressure mercury porosimetry are analytical techniques used to obtain this information. The high pressure mercury porosimetry provides more detailed information on the very small pores in the tens of nanometre size range. Nitrogen porosimetry provides more details on the pores in the larger size ranges. This information is used to ensure the quality of catalyst already in routine use as well as to evaluate new catalysts as they become available.

SAFETY CONSIDERATIONS:

1. Riffle sample in fumehood. Wear a dust mask and disposable gloves. While taking sample out from furnace, use proper gloves and tongs.
2. Wear safety glasses, face shield, or goggles; ear plugs; insulated gloves and apron; and hard hat in appropriate work areas.
3. When removing the filler rod from the sample tube, do not touch the filler rod with bare hands.

4. Do not touch the sample tube or the heating mantle until they have been allowed to reach room temperature. Touching the sample tube or mantle could result in personal injury, such as burns.

APPARATUS, REAGENTS, AND MATERIALS:

1. ASAP 2000 (Micromeritics Instrument).
2. UHP Nitrogen Gas Cylinder.
3. UHP Helium Gas Cylinder.
4. Liquid Nitrogen.
5. Analytical Balance ± 0.0001 g accuracy.

SAMPLE CONSIDERATIONS:

A 0.2 to 0.25 g of riffled sample is dried in a muffle furnace at 538°C for four hours. The sample is cooled in a vacuum desiccator.

PROCEDURE:

Calibration:

1. Recommended quantity per test: There are small differences among pellets. Between 10 and 14 pellets are needed to obtain a statistically reliable sample. A single pellet weighs about 0.05 g, so this means a sample weight of from 0.5 to 0.7 g.
2. Pertinent test conditions: Evacuate while heating at 250°C for three hours.
3. Reference sample of silica alumina can be used for instrument performance evaluation, whenever required. Reference sample port no. is 004-16821-00 of Micromeritics. Specific surface area of sample is 198±7 m^2/g.

Cleaning Glassware:

4. In order to obtain accurate analysis results, the glassware (sample tube, filler rod, etc.) must be clean. The following is recommended.
   a. Clean the sample tube and filler rod with warm, soapy water (using cleaning compound FL70 2% V/V dilution).
   b. Fill the ultrasonic unit with soapy water and put the sample tube and filler rod in it.
   c. Turn the ultrasonic unit on and leave the glassware in bath for 15 minutes.
   d. Using rubber gloves, remove the glassware from the ultrasonic unit and rinse them with hot water and with acetone.
   e. Dry the glassware in drying oven for two hours (oven temperature 110°C).

Equipment Check:

1. Check the liquid nitrogen level in each dewar. Add liquid nitrogen as necessary, using the dipstick provided to prevent over-filling.
   a. Dewar is filled from small liquid nitrogen tank (XC47/11), which is for use with ASAP 2000 only.
   b. Fill about half of ASAP 2000's liquid nitrogen tank from outside liquid nitrogen tank.
2. Check the supply of UHP nitrogen and helium. Change the cylinder if less than 200 psi shows on the gauge.

3. Check that the vacuum pump oil level in both de-gas and analysis pumps is between the lines. The oil level indicator is located at the back panel of the instrument.

SAMPLE ANALYSIS:

1. Weigh an empty sample tube with filler rod and seal frit to nearest 0.0001 g.
2. Weigh the tube with filler rod and seal plus the 0.2–0.25 g of sample, and use the work sheet to record all data.
3. Analysis of sample is done in two parts:
   a. De-gassing of sample.
   b. Analysis of sample.

Sample De-gassing:

Install the sample into a de-gas port using the following steps.

1. Remove the stopper from a de-gas port.
2. Place nut, ferrule, and O-ring on the sample tube.
3. Place sample tube on de-gas port. Tighten nut snugly by hand.
4. Place heating mantle on sample tube and put protective cover in place.
5. Note the de-gas Control Panel. Verify that the instrument is in Auto and the ready light is lit.
6. Set de-gas port temperature at 250°C.
7. Press the LOAD button. Verify that the LOAD button light is on.
8. Press the SELECT button each port (right, left) to be used; selection is verified when select light is on. If pressed twice, it will clear (null) selection.
9. Set the SLOW-FAST EVAC CROSSOVER to 500 millitorr.
10. Press temperature ENABLE button to start heating.
11. Press BEGIN to start loading procedure.
12. It will take about three to four hours for sample de-gassing. After the READY indicator is turned on, completion of sample de-gassing can be checked at any time during the run by pressing CHECK button, PORT button (right or left), and press BEGIN. If vacuum reading stays the same, it means de-gassing is complete. Any change in DE-GAS VACUUM GAUGE reading will indicate that moisture is still desorbing from the sample.

Unloading Sample After De-gassing:

1. Press ENABLE button to turn the heating off. Take the heater mantle off and let the sample tube come to room temperature; allow about 10 minutes.
2. Press UNLOAD button, PORT button (right or left port to be unloaded), and BEGIN button.
3. When ready light comes on, remove sample tube from de-gas port. Stopper the de-gas port.
4. Weigh the sample tube and record the weight on the data sheet.

Loading of Sample for Analysis:

1. Check liquid nitrogen levels in both dewars using a dipstick.
2. Slide insulating jacket down over the sample tube. Slide it down to touch the bulb.
3. Attach the sample tube to the analysis port in the same manner as when attaching to de-gas port.
4. Place dewar lid on sample tube just below port attachment. Lower protective cover.
5. Using the work sheet, enter the sample information using the following steps.
6. Press F3 twice from the Main Menu Screen to display screen. Add sample information.
7. Enter details about sample on Page 1. Press Pg Dn.
8. Enter Run Conditions Set Number 2 on Page 2. Set Number 2 has been pre-defined for hydrocracker catalyst. See operator's manual for details.
9. Enter Report Options Set Number 2 on Page 5.
10. Press F2 twice to return to the Main Menu.

Start the analysis as follows:

11. Press F7 from the Main Menu.
12. From the Start Run Screen, select Unit Number 1 and enter the sample number assigned to it.
13. Press Pg Dn. Then press Esc to return to the Main Function Menu.

CALCULATIONS: All calculations are performed by the computer controlling the instrument.

REPORT FORMAT: A final report summarizing the analysis results will be printed automatically. The results of several different calculation and calibration schemes are presented. The values to be reported for this method are the B.E.T. (Braunauer, Emmett and Teller) Surface Area and the N_2PV (Nitrogen Pore Volume). These values are found under the report headings B.E.T. SURFACE AREA and BJH (deBoer, Jura, and Harkins) DESORPTION, respectively. The value of the cumulative pore volume is to be reported for the N_2PV analysis.

PRECISION: Typical precision for surface area data indicates a present relative standard deviation of 1.2%. Typical precision for pore volume data indicates a percent relative standard deviation of 2.6%.

ACCURACY: Instrument accuracy is checked by analyzing the Micromeritics reference sample (198±7 m^2/g). Comparisons have also been made with external laboratories on specific samples.

6

MISCELLANEOUS

Quantitative Analysis of Refinery Gases by Gas Chromatography

INTRODUCTION: There are many gas chromatography-based schemes for the determination of "refinery gases." Most of these schemes are capable of generating equivalent results. Analysis times vary depending upon the level of resolution desired. The choice made, in this instance, of a procedure which utilizes a hydrogen transfer tube system results in a linear response to hydrogen over a wide concentration range. This, however, leads to an increased analysis time. For uses where the concentration of hydrogen is not expected to vary significantly from sample to sample, alternate systems with shorter analysis times may be appropriate.

SCOPE: This method determines the concentration (in terms of weight %) of the species listed below, present in gaseous samples.

Group 1 – Inorganic Gases	Group 2 – Organic Gases
Carbon Dioxide	Methane
Carbon Monoxide	Ethane
Hydrogen	Propane
Hydrogen Sulphide	Propylene
Nitrogen	*n*-Butane
	Isobutane
	n-Butene
	Isobutene
	trans-2-Butene
	cis-2-Butene
	1, 3-Butadiene
	n-Pentane
	Isopentane
	Cyclopentane
	C_{6+} (a conglomerate of all hydrocarbon species present of higher molecular weight than C_5)

SUMMARY:

1. This analysis is based upon a gas chromatographic separation of the various species listed previously. For ease of analysis each of the two groups, 1 and 2, is determined separately. The Carle 311 Analytical Gas Chromatograph houses two separate chromatographic systems with their own sample loops, columns, valves, and detectors. Therefore, to obtain information on all of the species, it is necessary to submit, in pressure bombs, two samples or a sufficiently large quantity of sample for both analyses. Typical sample volumes injected per run are dependent upon which column system the sample travels through. Both systems are equipped with gas sampling loops. The sampling loop, which is eventually terminated by the thermal conductivity detectors (TCD) of system 1, has a volume of 1.0 mL. The sample loop connected to system 2, which leads to the flame ionization detector (FID) has a volume of 250 µL.
2. Group 1 species are analyzed by a two column chromatographic system. Figure 1 is a schematic of this system. The gas sample is injected with the columns coupled in series. Column 1, packed with 80% Porapak N and 20 Porapak Q, allows the light components to enter column 2,

packed with the 13X molecular sieve, while retaining CO_2 and those species present which would elute later than CO_2. The hydrogen present in the sample travels through column 2 to the hydrogen transfer tube.

3. Based on the unique permeability properties of palladium, the hydrogen transfer tube system (HTS) selectively transfers hydrogen from a helium carrier gas stream to a nitrogen carrier gas stream. Measuring hydrogen in a nitrogen carrier yields more precise results over larger concentration ranges than can be achieved with helium carrier gas.
4. The hydrogen passes through the hydrogen transfer tube system rapidly and is the first component peak recorded. The first thermal conductivity detector is a nitrogen carrier gas detector and is used only for the detection of hydrogen. The columns are then uncoupled; column 1 is coupled to the second thermal conductivity detector while column 2 containing any oxygen, nitrogen, methane, and carbon monoxide present in the sample is isolated from the flow system. This is illustrated in Figure 2. Components lighter than C_3 are then eluted directly from column 1 to the detector. These species are carbon dioxide, ethane, and hydrogen sulphide. After the hydrogen sulphide has eluted, column 1 is backflushed to an external vent and column 2 is coupled to the detector (Figure 3). Although both methane and ethane may be eluted, this chromatogram is not used to analyze for these two components. They are more accurately assayed with the group 2 species.
5. Group 2 species are analyzed by a multi-column chromatographic system. The first column, column 3, is packed with OPN on Porasil C. Basically this column separates on the basis of carbon number. The timing sequence is set to allow the passage of all species below C_6 to column 4. This is illustrated in Figure 4. After the species below C_6 have entered column 4, the sequence of the columns is reversed. The resultant configuration, Figure 5, leads to components C_6 and above being eluted directly to the flame ionization detector as a single unresolved peak. Columns 4 and 5, packed with bis-adipate and squalene on Chromosorb P-AW and OPN on Porapak C, respectively, resolve the components less than C_6 on the basis of both carbon number and saturation. Column 6, packed with 28% DC 200/500 on Chromosorb P-AW, is a small guard column placed directly in front of the detector to prevent elution of large hydrocarbon contaminants.
6. Each column system is calibrated with a carefully selected certified standard mixture. The composition of each standard is chosen to approximate the concentrations of the species of interest in the sample. Therefore, major changes in sample composition necessitate major changes in standard composition.
7. Quantitative results are obtained from the measured areas of the recorded peaks and the application of individual response factors.

BACKGROUND:

Many of the off-gas streams in the Syncrude upgrading plant are monitored routinely to provide for safe and reliable operation of the plant, assessment of overall unit performance, and, in some instances, to allow determination of fuel gas quality.

SAFETY CONSIDERATIONS:

1. Caution should be used when handling compressed gas cylinders. Cylinders must be securely belted in a cylinder holder attached to a wall

Schematic of Channel 1: Detection of Inorganic Gases

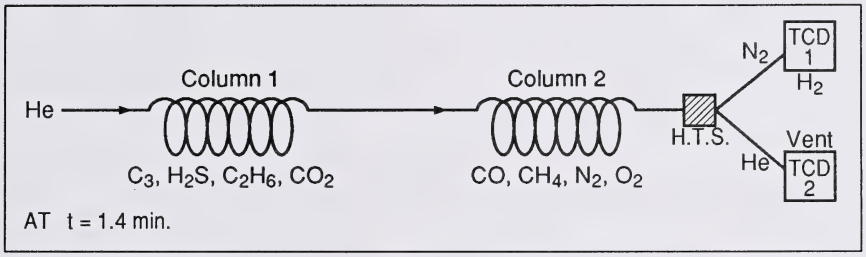

Figure 1.

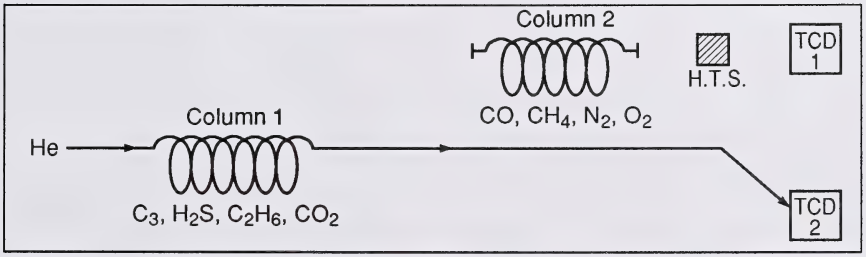

Figure 2.

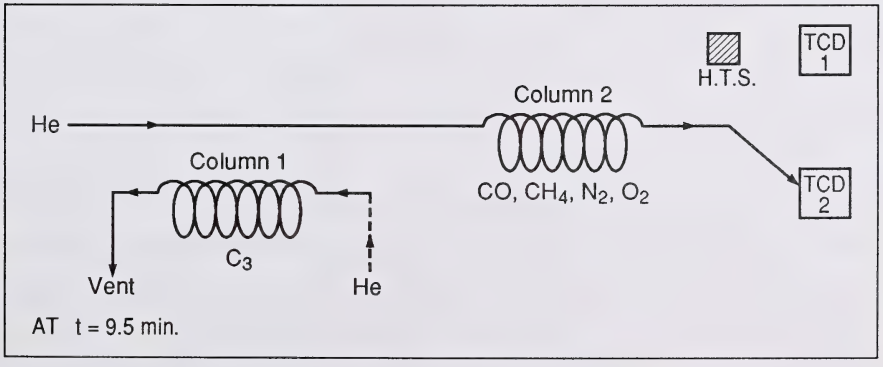

Figure 3.

Schematic of Channel 2: Detection of Organic Gases

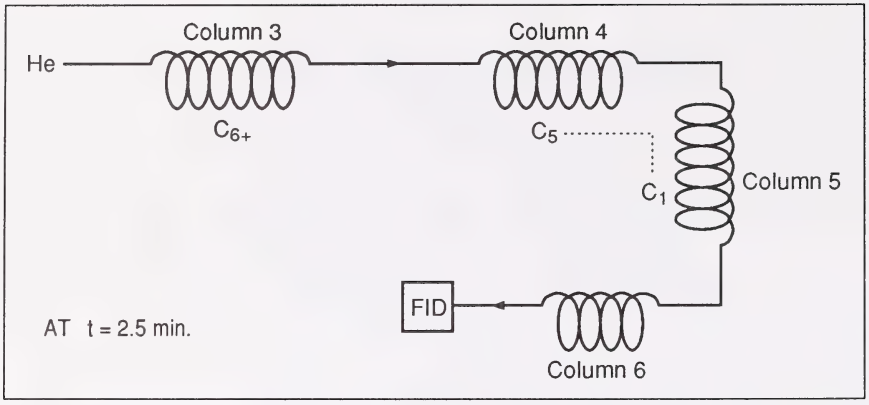

Figure 4.

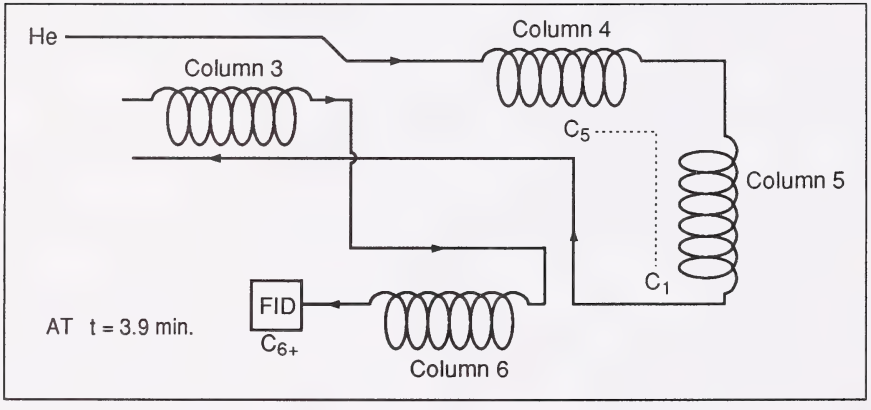

Figure 5.

or lab bench when in use. The cylinder cap must be firmly in place when cylinders are moved.

2. Hydrogen: highly flammable and explosive; ensure that hydrogen lines are leak-free; non-toxic.
3. Carbon Monoxide: highly flammable; dangerous fire and explosion risk; highly toxic by inhalation.
4. Hydrogen Sulphide: highly toxic by inhalation; strong irritant to eyes and mucous membranes; highly flammable.
5. Butadiene: highly flammable; may form explosive peroxides on exposure to air; moderately toxic; irritant to eyes and mucous membranes.
6. Butane: highly flammable; dangerous fire and explosion risk; asphyxiant gas.

7. *n*-Butene: highly flammable; dangerous fire and explosion risk; asphyxiant gas.
8. Isobutene (2-methylpropene): highly flammable; dangerous fire and explosion risk.
9. *Cis*-2-butene: highly flammable; dangerous fire and explosion risk; asphyxiant gas.
10. *Trans*-2-butene: highly flammable; dangerous fire and explosion risk: asphyxiant gas.
11. Ethane: severe fire risk if exposed to sparks or open flame.
12. Methane: severe fire and explosion hazard.
13. *n*-Pentane: highly flammable; moderately toxic by inhalation; tolerance 50 ppm in air.
14. Cyclopentane: highly flammable; moderately toxic by ingestion and inhalation.
15. Isopentane: highly flammable.
16. Propane: highly flammable; moderately toxic by inhalation.
17. Propylene: highly flammable; low toxicity.

APPARATUS, REAGENTS,

1. Carle Analytical Gas Chromatograph, AGC 311H, fitted with the following:
   - hydrogen transfer system (HTS)
   - special dual thermal conductivity detectors (TCD)
   - very high sensitivity flame ionization detector (FID)
2. Column 1–6' (1.83 m) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with 80% Porapak N and 20% Porapak Q (50–80 mesh)
3. Column 2–7' (2.14 m) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with 13X molecular sieve (45–60 mesh)
4. Column 3–2' (0.61 m) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with OPN on Porasil C (80–100 mesh)
5. Column 4–21' (6.40 m) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with 19.3% bis-adipate and 3.3% squalene on Chromosorb P-AW (45–60 mesh)
6. Column 5–11' (3.35 m) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with 2.25% OPN on Porapak C (80–100 mesh)
7. Column 6–4' (101.6 mm) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with 28% DC 200/500 on Chromosorb P-AW (60–80 mesh)
8. Column 7–3' (0.91 m) by 1/8" (3.175 mm) O.D. stainless steel tubing packed with 13X Molecular Sieve (80–100 mesh)

All seven columns may be purchased packed from Technical Marketing Associates.

9. Helium, high purity, Matheson
10. Nitrogen, oxygen-free, Matheson.
11. Hydrogen, zero gas, Matheson.
12. Air, zero gas, Matheson.
13. Calibrating Mixtures (exact composition may vary slightly from lot to lot):

- Certified Standard 1 (Matheson) consisting of:
  1.00% carbon dioxide
  4.93% hydrogen sulphide
  1.00% carbon monoxide
  0.51% nitrogen
  Balance hydrogen.

- Certified Standard 2 (Matheson) consisting of:
  0.521% carbon dioxide
  77.98% hydrogen sulphide
  0.516% carbon monoxide
  1.08% nitrogen
  19.9% hydrogen.

- Certified Standard 3 (Matheson) consisting of:
  0.892% methane
  0.944% ethane
  0.947% propane
  1.037% isobutane
  1.036% *n*-butane
  0900% isopentane
  0.714% *n*-pentane
  1.075% 1-butene
  1.071% isobutene (2-methylpropene)
  0.781% *cis*-2-butene
  0.878% *trans*-2-butene
  0.775% 1,3-butadiene
  0.979% propylene
  0.914% cyclopentane
  Balance hydrogen.

14. 5 mL gas sampling syringe — Precision Sampling Corporation, pressure-lok series A-2, Cat. No. 050036.
15. Stainless steel sample cylinders: Whitney sample cylinders DOT3E 1800.
16. Quick connect fittings: Swagelok QC4 D200 and QC4 Bl 400.
17. Carrier gas purifier: Supelco 2-3800.
18. Replacement cartridges for above: Supelco 2-2398

SAMPLE CONSIDERATIONS:

Amount Required: 10 psi (~70 kPa) in approximately 150 mL bomb

Properties: Homogeneous gas sample

Interferences: Any unidentified (unexpected) species present in the sample which has the same or similar retention time as one of the expected species would be considered as that

species. For example, ethane (expected) has a retention time of 5.93 minutes while ethylene (unexpected) has a retention time of 6.00 minutes. In a sample which contains ethylene but no ethane, any ethylene present may be reported as ethane. The originator of the sample should be aware of potential interferences.

Destructive: Yes

PROCEDURES: Gas Chromatographic Configuration and Flow Rates

1. The configuration of the columns within the Carle Analytical Gas Chromatograph is shown in Figure 6. The carrier gas flow rate depends upon the location within the gas chromatograph. The procedure given below for checking and setting flowrates need only be carried out once every six months. Extreme care must be used when setting flowrates to ensure that the valve timings set are compatible with the flow rates. (They will be compatible if set exactly as specified).
2. Nitrogen flow, which is sweeping the hydrogen from the hydrogen transfer tube, and carrying it through TCD 1, is set to flow at a rate of approximately 55 mL/min (50 psi (344.75 kPa(g) at the regulator).

The helium flow rate is set in stages:

3. Turn power off to FID system.
4. Remove the FID chimney and close the lid to the detector compartment.

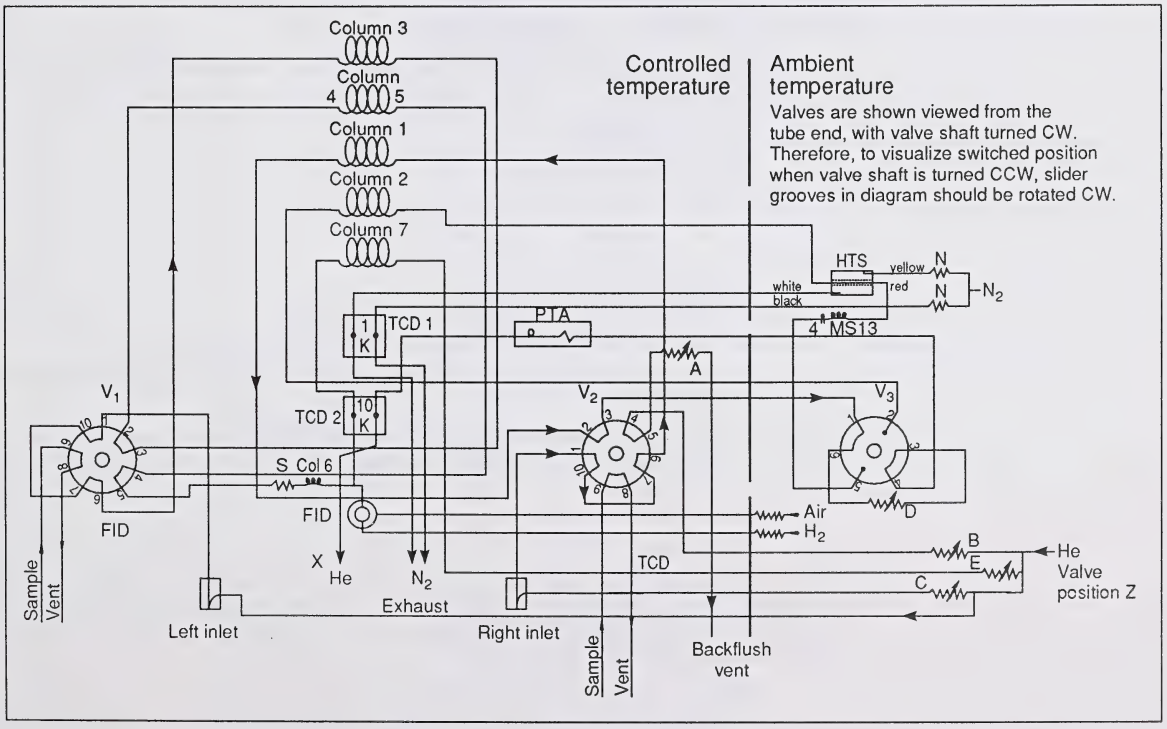

Figure 6. Carle 311 plumbing schematic.

5. Turn off hydrogen and air flows.
6. With the flow probe, measure the flow at the detector jet with restrictor E closed (see Figure 6). Set the helium regulator (located at the left of the g.c.) so that the flow measured here is 28 mL/min.
7. Now adjust restrictor E to give a flow of 55 mL/min.
8. Replace FID chimney.
9. With V_2 (Valve 2) turned clockwise (position 2) and V_3 (Valve 3) turned counterclockwise (position 1), set the helium flow at point X (see Figure 6) at 28 mL/min. Use restrictor C to set this flow.
10. Turn V_3 (Valve 3) clockwise (position 1). Set the helium flow at point to 28 mL/min using restrictor D.
11. Turn V_2 (Valve 2) counterclockwise (position 2). Using restrictor B, set the helium flow at point X to 28 mL/min.
12. With the valve configuration V_2 counter-clockwise and V_3 clockwise measure the flow at the backflush vent. Using restrictor A, set this flow to 33 mL/min.

    Care should be taken when checking these flow rates. Any deviations will result in altered times. The valve-timing has been factory-set, utilizing these exact flow rates.

Start-up:

13. Ensure both helium and nitrogen carrier gases are flowing. These must be set to flow whenever the oven temperature is above room temperature.
14. Ensure column temperature is set at 58°C.
15. Ensure that the control settings on the g.c. are set as follows:

    TCD

    - left column
    - output = 1

    FID

    - range 10
    - output = 2
16. Turn on air and hydrogen at cylinder head.
17. Turn on the TCD by switching the bridge setting to thermistors.
18. Turn on the hydrogen transfer system heater and set temperature to 550±10°C.

    Caution: Do not allow the hydrogen transfer system temperature to exceed 600°C. Permanent damage to the system may result from overheating.

Calibration:

19. Calibration must be carried out on each channel each day that samples are analyzed. If the instrument has not been used for two days or more, then inject and run each standard through the appropriate channel once prior to the calibration.
20. The calibration standards must be chosen such that the concentrations of the various species of interest approximate the concentration expected in the sample.

21. The exact concentrations of each of the species in the standards must be stored in the SP4100 integrator's memory. The data are currently stored in files within the SP4100's.

    File 1 Certified Standard 1 (TCD)

    File 2 Certified Standard 2 (TCD)

    File 3 Certified Standard 3 (FID)

    The data must be updated each time a new standard is utilized.

22. Connect the appropriate Certified Standard to the appropriate sample injection fitting:

    TCD Group 1 – Inorganic Gases

    FID Group 2 – Organic Gases

23. Check the baseline level; set it to 1000±3.

24. Open the Certified Standard cylinder. Set the regulator to 20 psi (137.90 kPa (g)) and ensure that the standard is flowing through the sample loop by observing the movement of the float in the flowmeter.

25. Close the Certified Standard cylinder and as soon as the flow stops on the flowmeter, actuate the injection of the calibration mixture by keying in:

    CALIB

    INJECT/STANDBY

    It is essential that the flowmeter be observed carefully and that the injection valve is actuated as soon as the flow through the flowmeter is observed to stop. This ensures that the same volume of sample at the same pressure is introduced into the gas chromatograph with every injection.

26. The response factors for the species whose concentrations are stored in SP4100's are automatically calculated and stored for later use.

27. Check the report generated to ensure correct peak identification. Ensure that a response factor has been calculated for each injected species.

28. Keep a careful record of the retention times and response factors in the log book.

29. The FID channel is also used for the determination of C_{6+} hydrocarbons. None of these species is present in the standard. Therefore it is necessary to determine type RF value using the following formula as specified in ASTM D1945, "Method for Analysis of Natural Gas by Gas Chromatography."

$$RF\ C_{6+} = \left(average\ RF\ C_5\right) \frac{molecular\ weight\ C_6}{molecular\ weight\ C_5}$$

$$= \left(average\ RF\ C_5\right) \frac{86}{72}$$

30. After the RF value for C_{6+} has been determined it must be entered into the SP4100 in the following manner:

    RF (1) = calculated RF value ENTER

Sample Analysis:

The samples must be analyzed on the day they are submitted. The procedure for the analysis of a sample is very similar for each channel. Each

sample must be run on both channels. Since each channel is equipped with its own integrator, both channels can be run at the same time. In order to minimize turn-around time, inject the sample into the FID channel first and then into the TCD channel.

31. Allow the TCD channel sufficient time from cold start for the hydrogen transfer system (HTS) to reach operating temperature.
32. Zero baseline to 1000±3 using the coarse zero knob located on top of the chromatograph for each channel.
33. Connect sample to appropriate sample inlet, either FID or TCD.
34. Open sample bomb.
    - Ensure that the sample is flowing through the sample loop by observing the movement of the float in flowmeter.
    - Close sample bomb.
    - Depress INJECT/STANDBY as soon as the flow stops on the flowmeter.
    - Wait for the sample valve to actuate then disconnect the sample bomb from the injection line.
35. When the run is complete the appropriate integrator will immediately print a report. The concentrations of the species present in the sample will be automatically calculated if they have been calibrated. On the TCD channel these species are:
    - hydrogen (H_2)
    - carbon dioxide (CO_2)
    - hydrogen sulphide (H_2S)
    - nitrogen (N_2)
    - carbon monoxide (CO).
36. On the FID channel the species automatically calculated are:
    - C_{6+}
    - methane
    - ethane
    - propane
    - propylene
    - *i*-butane (isobutane)
    - *n*-butane
    - *n*-butene (1-butene)
    - *i*-butene (isobutene or 2-methylpropene)
    - t2-butene (*trans*-2-butene)
    - c2-butene (*cis*-2-butene)
    - butadiene (1, 3-butadiene)
    - *i*-pentane (isopentane)
    - *n*-pentane
    - *c*-pentane (cyclopentane)

Shut-down:

37. Turn off hydrogen and air flow to FID.

38. Turn TCD thermistors to OFF.
39. Turn hydrogen transfer system (HTS) heater to OFF.

CALCULATIONS:

1. The species calibrated, each have a response factor RF_A:

$$RF_A = \frac{Peak\ Area\ A_{Calibration\ Run}}{Concentration\ A_{Calibration\ Standard}}$$

2. The response factor for C_6+ is estimated as:

$$RF\ C_{6+} = \left(average\ RF\ C_5\right) \frac{molecular\ weight\ C_6}{molecular\ weight\ C_5}$$

3. The concentration of each species is calculated as:

$$A = \frac{Peak\ Area_A}{RF_A}$$

REPORT FORMAT: The results are reported in terms of mole-percent to the nearest 0.01.

TIME CONSIDERATIONS:

Time Per Analysis:	45 min
Technologist Contact Time:	15 min
Samples Per Time Period:	9/d
Calibration Time:	45 min

PRECISION: Precision evaluations of the reproducibility of the analytical system have been carried out using multiple injections of a certified gas standard. These are tabulated in Table 1.

Table 1. Reproducibility of concentration results

Observed concentrations %: Day 1

Species	True conc.	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Average
TCD Channel Hydrogen	92.56	93.35	93.13	92.90	92.83	93.21	93.36	92.87	93.09±0.23
Carbon Dioxide	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Hydrogen Sulphide	4.93	4.94	4.95	4.94	4.95	4.96	4.95	4.95	4.95±0.01
Nitrogen	0.51	0.50	0.50	0.51	0.50	0.50	0.50	0.50	0.50±0.01
Carbon Monoxide	1.00	1.00	1.01	1.02	1.02	1.00	1.01	1.00	1.01±0.01
FID Channel Methane	0.892	0.890	0.887	0.886	0.887	0.887	0.905	0.892	0.891±0.007
Ethane	0.944	0.941	0.938	0.938	0.940	0.943	0.944	0.942	0.941±0.002
Propane	0.947	0.943	0.941	0.941	0.943	0.950	0.947	0.945	0.944±0.003
Propylene	0.979	0.976	0.974	0.974	0.975	0.982	0.979	0.976	0.977±0.003
Isobutane	1.037	1.034	1.030	1.032	1.032	1.043	1.038	1.034	1.035±0.004
n-Butane	1.036	1.034	1.031	1.031	1.032	1.047	1.034	1.033	1.035±0.006
n-Butene	1.075	1.073	1.037	1.038	1.038	1.041	1.076	1.036	1.048±0.018
Isobutene	1.071	1.062	1.058	1.058	1.057	1.098	1.065	1.067	1.066±0.014
trans-2-Butene	0.878	0.875	0.873	0.873	0.873	0.891	0.875	0.876	0.877±0.007
cis-2-Butene	0.781	0.779	0.819	0.819	0.818	0.834	0.818	0.819	0.815±0.017
Butadiene	0.775	0.772	0.728	0.728	0.728	0.744	0.729	0.713	0.735±0.019
Isopentane	0.900	0.896	0.892	0.893	0.893	0.912	0.898	0.892	0.897±0.007
n-Pentane	0.714	0.707	0.710	0.709	0.710	0.727	0.713	0.711	0.712±0.007
Cyclopentane	0.914	0.906	0.903	0.904	0.907	0.934	0.910	0.906	0.910±0.011

Observed concentrations %: Day 2

Species	True conc.	Run 1	Run 2	Run 3	Run 4	Run 5	Average
TCD Channel	92.56	92.94	93.03	93.07	92.95	92.57	92.91±0.20
Carbon Dioxide	1.00	1.01	1.02	1.01	1.01	1.00	1.01±0.01
Hydrogen Sulphide	4.93	4.97	4.98	4.96	4.97	4.96	4.97±0.01
Nitrogen	0.51	0.48	0.49	0.48	0.48	0.49	0.48±0.01
Carbon Monoxide	1.00	0.99	1.01	0.97	1.02	1.00	1.00±0.02
FID Channel Methane	0.892	0.894	0.893	0.896	0.896	0.898	0.895±0.002
Ethane	0.944	0.946	0.946	0.948	0.948	0.949	0.947±0.001
Propane	0.947	0.949	0.949	0.951	0.951	0.953	0.951±0.002
Propylene	0.979	0.982	0.980	0.983	0.982	0.984	0.982±0.002
Isobutane	1.037	1.038	1.037	1.040	1.040	1.041	1.039±0.002
n-Butane	1.036	1.037	1.036	1.038	1.038	1.039	1.038±0.001
n-Butene	1.075	1.076	1.004	1.042	1.042	1.043	1.042±0.026
Isobutene	1.071	1.072	1.075	1.070	1.071	1.073	1.072±0.002
trans-2-Butene	0.878	0.879	0.881	0.878	0.879	0.878	0.879±0.001
cis-2-Butene	0.781	0.781	0.826	0.821	0.824	0.824	0.810±0.019
Butadiene	0.775	0.775	0.7334	0.732	0.733	0.733	0.741±0.019
Isopentane	0.900	0.934	0.892	0.899	0.896	0.896	0.903±0.017
n-Pentane	0.714	0.714	0.712	0.714	0.714	0.714	0.714±0.001
Cyclopentane	0.914	0.915	0.911	0.911	0.916	0.915	0.914±0.002

Observed concentrations %: Day 3

Species	True conc.	Run 1	Run 2	Run 3	Run 4	Average
TCD Channel Hydrogen	92.56	92.31	92.32	92.28	92.44	92.34 ±0.07
Carbon Dioxide	1.00	0.95	0.94	0.93	0.94	0.94 ±0.01
Hydrogen Sulphide	4.93	4.59	4.62	4.56	4.58	4.59 ±0.03
Nitrogen	0.51	0.44	0.43	0.44	0.44	0.44 ±0.01
Carbon Monoxide	1.00	0.98	0.97	0.98	0.99	0.98 ±0.01
FID Channel Methane	0.892	0.905	0.888	0.887	0.893	0.893 ±0.008
Ethane	0.944	0.958	0.941	0.938	0.944	0.945 ±0.009
Propane	0.947	0.962	0.943	0.941	0.947	0.948 ±0.010
Propylene	0.979	0.955	0.976	0.974	0.978	0.981 ±0.010
Isobutane	1.037	1.049	1.034	1.031	1.035	1.037 ±0.008
n-Butane	1.036	1.048	1.034	1.031	1.033	1.037 ±0.008
n-Butene	1.075	1.132	1.073	1.047	1.037	1.072 ±0.043
Isobutene	1.071	1.075	1.062	1.066	1.065	1.067 ±0.006
trans-2-Butene	0.878	0.891	0.875	0.871	0.880	0.879 ±0.009
cis-2-Butene	0.781	0.787	0.799	0.770	0.782	0.780 ±0.007
Butadiene	0.775	0.835	0.779	0.734	0.734	0.771 ±0.048
Isopentane	0.900	0.909	0.896	0.892	0.893	0.989 ±0.008
n-Pentane	0.714	0.720	0.707	0.710	0.709	0.712 ±0.006
Cyclopentane	0.914	0.919	0.906	0.903	0.904	0.908 ±0.007

Note: The data normally reported to two decimal places, the third is carried here for illustrative purposes.

7

APPENDIX

The Syncrude-AOSTRA Air Quality Prediction System (AQPS) – An Early Warning System for Air Quality

SUMMARY: The Syncrude-AOSTRA Air Quality Prediction System (AQPS) is a computer model to predict the quality of air in the vicinity of an industrial plant. It is an automated real-time measurement and computation system capable of forecasting local pollutant concentrations at ground level up to 24 hours ahead of time. The prediction techniques were deliberately chosen for their reliability.

The AQPS has four major components:

- a stack emission monitor
- a network of air quality monitors on the ground
- meteorological instrumentations
- the forecast facility

The following prediction schemes are used in the AQPS:

- concentration trend extrapolation
- dispersion calculations
- historical comparisons
- a composite forecast using all the above techniques

INTRODUCTION: The uncontrolled burning of sulphurous fossil fuel in an industrial plant results in the emission of large quantities of sulphur dioxide normally discharged from a tall stack. Under certain atmospheric conditions these emissions will result in occasionally exceeding the legal limits for maximum ground level concentration of sulphur dioxide.

Most North American industrial plants emitting waste gases into the atmosphere, are required by law to monitor the air quality in their immediate area (1,2).

Pollutant upper limits are set by legislation. Because any practical network of air monitor stations cannot provide blanket coverage for the area of concern, it is not uncommon for a company to perform air quality calculations from time to time to check that pollutant concentrations in between the monitor stations are within acceptable limits. The model calculations become especially important when plant emissions are unusually large for any reason.

The Air Quality Prediction System described herein has been designed as a tool to aid air quality management.

The most useful air quality calculations are made before a release occurs, while there is still time to modify the emissions if their potential consequences turn out to be unacceptable. Such calculations are predictive and air quality management decisions based on these calculations are pro-active.

Model calculations are of little practical use if they are made after the emission has taken place. The best that can be expected in such cases is that the inevitable consequences of a known emission can be estimated before they have fully developed, and reactive steps can be taken, if necessary, to ameliorate any adverse effects.

The objective of the AQPS project was to design and build an automated real-time measurement and computation system able to forecast local sulphur dioxide ground level concentration up to 24 hours before they occur.

Emphasis was placed on using prediction techniques that were practical, reliable, and realistic. These techniques are then applied in models driven by relevant, up-to-date, and accurate input data. This means that the AQPS must incorporate a well-chosen combination of time-proven and state-of-the-art measurement and modeling technologies.

Intended Application: Air Quality Forecasts

The main purpose of the AQPS is to give an early warning when impending weather conditions are conducive to high ground level sulphur dioxide concentrations within 50 km of an industrial installation. Once an hour, the AQPS forecasts air quality at locations currently affected by the plume. The AQPS also predicts location and magnitude of the constantly moving point of maximum ground level concentration under the plume, and estimates the extent of the plume "footprint" centered on this point, within which the concentration is expected to be above the legal limit. Forecasts of the one-hour average concentration footprint are made 1, 2, 4, and 6 hours ahead of time, and an hourly forecast of the 24-hour average concentration footprint is made 12 and 24 hours in advance.

Inherent System Limitations

There are several important limitations to the forecasting ability of the AQPS. First, the system gives an early warning of air quality exceedances only over the short term; e.g., predictions of the one-hour average concentration can be made only up to eight hours in advance. This means that the relatively short-range AQPS described here is of limited use in solving acid deposition and other transport problems over long distances. Secondly, the accuracy of forecasts decreases with lead time, so that only the 24-hour average concentration forecast is useful 12 or 24 hours in advance.

The AQPS also needs sophisticated technology to provide plume level input data necessary for realistic forecasts. Most industrial plants today are required by law to operate a Continuous Stack Emission Monitor (CSEM) and an Air Monitor Network (AMN). Both of these hardware items are essential for the operation of the AQPS. However, there is no similar requirement to monitor the weather conditions that carry the plume from the CSEM to the AMN. As a consequence, few plants have the weather instruments or technical personnel needed to provide input data for a modern AQPS like the one described here. This is perhaps the single most important obstacle to rapid and widespread adoption of available AQPS technology.

Components of the Prediction System

A. The AQPS Structure:

The AQPS has the following major components:

i. The Continuous Stack Emission Monitor (CSEM) which measures and reports temperature and velocity of the total gases going up the stack and the concentration of SO_2 therein.

ii. The Air Monitor Network (AMN) which measures and reports SO_2 concentrations from strategically-placed instruments around the plant.

iii. A network of meteorological monitoring instruments that provides pertinent atmospheric dispersion parameters.

iv. An AQPS Central Forecast Facility (CFF) serviced by:
- a computer to run the model,
- an environmental specialist to ensure continuous and reliable operation of the system and to issue forecasts,
- an air quality modeler to improve model components and accuracy and reliability of weather sensors.

v. A man/machine prediction-decision strategy which provides for rational decisions and reactions based on the analysis of all available information.

B. The AQPS Design:

A simplified schematic of the AQPS concept and design is shown in Figure 1.

The sequence of steps following release of pollution is given, with measured stack emissions carried and dispersed by observed weather conditions to produce measured concentrations at the AMN stations.

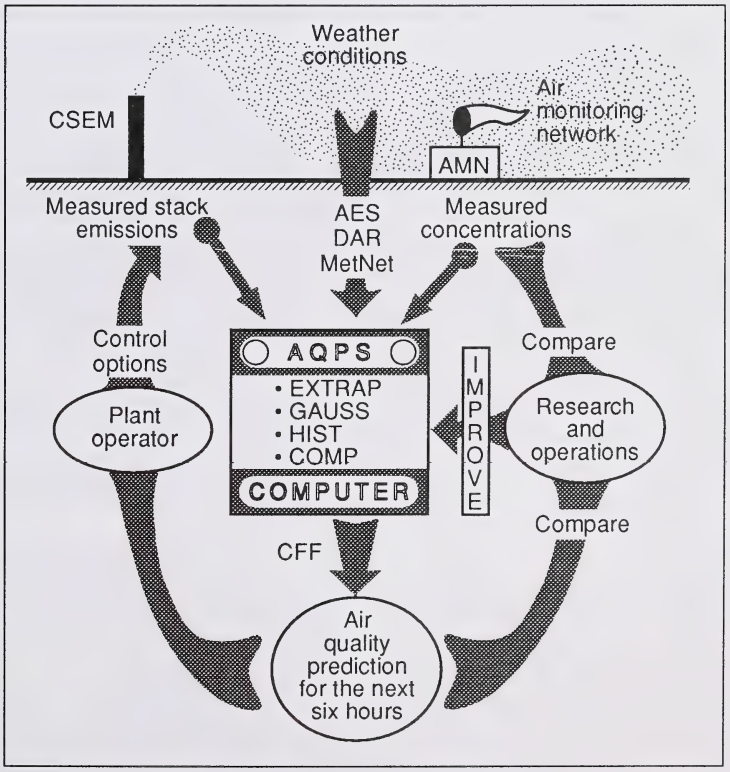

Figure 1. AQPS concept and design.

The AQPS operating cycle begins with emissions, weather, and AMN data being sent to the AQPS computer in the CFF. The computer combines three independent prediction techniques to provide a single composite air quality forecast, which tends to moderate spurious extremes that any one submodel can occasionally produce.

The requirement for improving the system, including verification and analysis of results and the application of the latest state-of-the-art models and techniques, was acknowledged early in the project. As shown in the action loop on the right of Figure 1, the CFF personnel work with and are supported by an AQPS Development Group, whose role is to measure AQPS performance and identify weaknesses by regularly comparing the details of composite forecasts and submodel predictions with actual weather and AMN data. This group develops and implements improvements to the AQPS instrumentation and model software as necessary.

In the action loop to the left, plant operators vary the emissions as appropriate, based in part on the air quality information they obtain from the AQPS forecasts.

Air Quality Prediction Schemes

Experience with weather prediction and air quality models has shown that forecast accuracy is not consistent from hour to hour and day to day when the forecast is based on just one prediction scheme. Sometimes a single model does well, and other times it misses reality by several orders of magnitude. To minimize this problem the present AQPS is based on more than one modeling technique. This multi-faceted approach to real-time air quality forecast systems was first developed for the copper smelter industry in the USA (3).

The prediction schemes used in the present system are designed to ask and answer the following questions:

1. Trend Extrapolation (at the AMN stations): "What will happen to air quality if the present short-term ground level concentration trends continue?"
2. Physical-Mathematical Model (valid at any point): "What do the dispersion equations predict will happen?"
3. Historical Comparisons (at the AMN stations): "What happened to air quality when emissions and weather were previously like they are now?"
4. Composite Prediction: A weighted average of the three independent predictions obtained above.

These techniques are now discussed.

Trend Extrapolation:

Extrapolation has long been a standard technique for meteorological prediction. There is no reason why, in principle, extrapolation cannot also be applied to air quality prediction.

The process of extrapolation is based on the premise that current data trends will persist long enough to provide a useful guide as to what the near-term future holds for the parameter in question. Its application to weather prediction and air quality forecasting remains useful so long as the forces controlling wind patterns, boundary layer mixing, and other dynamic

influences in the atmosphere are constant or change at a reasonably slow rate. The accuracy and reliability of the extrapolation method generally deteriorates as the projection is forced deeper into the future. It is especially susceptible to error when discontinuities occur in the atmosphere such as frontal passages and inversion break-ups. Thus there are many phenomena which can terminate an old trend and initiate a new trend. This is the single largest drawback with meteorological extrapolation.

Forecasters have long recognized the limitations of extrapolation and have used the method cautiously. Nevertheless, experience with and testing of full time supplementary emission control systems in the USA have shown that ground level concentrations appear to exhibit both short-term and medium-term cycles associated with wind and turbulence variations which can be successfully extrapolated over periods of several hours (3).

Physical-Mathematical Model:

The physical-mathematical model, which is a modified Gaussian dispersion model, combines within one theoretical framework the most important aspects of the phenomena of plume rise, dispersion, thermal stratification, and atmospheric turbulence (4). The model is based in part on knowledge gained from recent investigations of flow within free shear layers and must be considered state-of-the-art.

The model calculates the ground level concentration at discrete locations from a given set of emission and weather conditions. The model requires atmospheric data for each 50 m thick air layer from surface up to some 600 m above ground (the normal range of an industrial chimney plume).

The major limitation of this physical-mathematical model is its requirement for high quality meteorological input data.

A second limiting factor is our decision to model the atmosphere as a series of independent uniform layers, each 50 m thick. This approach is normally a reasonable one, but in extreme cases, such as when the wind direction shifts by more than one degree per metre of height, the assumption breaks down and so does model accuracy.

Before the physical-mathematical model can make an air quality prediction, it needs a forecast of wind speed and direction, turbulence level, and temperature profile expected during the next several hours. Historical comparisons (the next topic for discussion) could be used to predict the needed input as can the extrapolation scheme.

Historical Comparisons:

The purpose of the "historical" approach is to identify, from a historical data base, situations which are similar to the present meteorological and air quality situation. The scheme is based on an understanding of the physical relationships and interactions among ground level concentration, stack emission, and topographical, micrometeorological and synoptic scale features in the vicinity of the plant as well as the broad circulation pattern and dynamic characteristics of the upper atmosphere. The historically similar data records are then used to forecast weather input for the physical-mathematical model and, most importantly, the pollutant concentrations at the monitor stations.

The principal weakness of the historical scheme is that it will require one or two years of data collection before it is fully effective.

Composite Forecast:

Traditional dispersion models have unimpressive records when predicting ground level concentrations on a real-time basis. The development of a trustworthy real-time physical-mathematical model for air quality prediction remains an ongoing process. No single model is yet suitable for stand-alone use in real-time air quality prediction. The AQPS thus consists of an integrated model which utilizes all of the above submodels. As discussed earlier, these models make use of a combination of real-time emissions, meteorological and air quality measurements, and a historical data base of these variables.

The composite forecast produces a weighted average of the various forecast methods and in so doing provides a forecast at each of the AMN stations. The weighting factors in the equation are chosen based on testing, experience, and operational requirements and can be changed (automatically) based on the effectiveness of each of the prediction methods for a given forecast period.

System Validation:

AQPS technology is still in its infancy and undoubtedly there will be many modeling weaknesses, omissions, errors, and software bugs discovered during the early period of AQPS operation. These can be found and corrected only by a systematic validation procedure in which all AQPS predictions are carefully tested against the actual AMN concentrations (5). The fairly intensive process of system error identification and correction may take as long as one to two years depending on available manpower. Nevertheless, to ensure that the system maintains credibility as a forecasting tool, system validation must be given high priority by those responsible.

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